FILE DESCRIPTION

NEW YORK FILE

Bulky Exhibits

SUBJECT A. BROTHMAN

FILE NO. 100-95068

VOLUME NO.

SERIALS 1B 100 ONLY

NOTICE

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JULIUS ROSENBERG, et a

NEW YORK BULKY EXHIBIT FILES

A. Kaufman

65-45056 1B100 only

Exhibit Number	Description	Released	Denied	Withheld
100	miscellaneous papers	✓		
100	Photographs			not [illegible]

FD-141
(7-1-48)

BULKY EXHIBIT

Date received 11/16/50

ABRAHAM BROTHMAN

100-95068-1B
(Title of case)

Submitted by Special Agent JOHN M. COLLINS

Source from which obtained Phila. Office- FBI

Address

Purpose for which acquired INVESTIGATION

Location of bulky exhibit IN CABINET WITH FILE

Estimated date of disposition TO BE DECIDED AT CONCLUSION OF CASE

Ultimate disposition to be made of exhibit RETAIN

List of contents:

100. Fifteen envelopes containing miscellaneous papers and blue prints found during a search of Gold's home by S.A. Fred C. Birkley of the Phila. office.

(57)
100-95068-1B

SAC, Philadelphia 6/23/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

#1

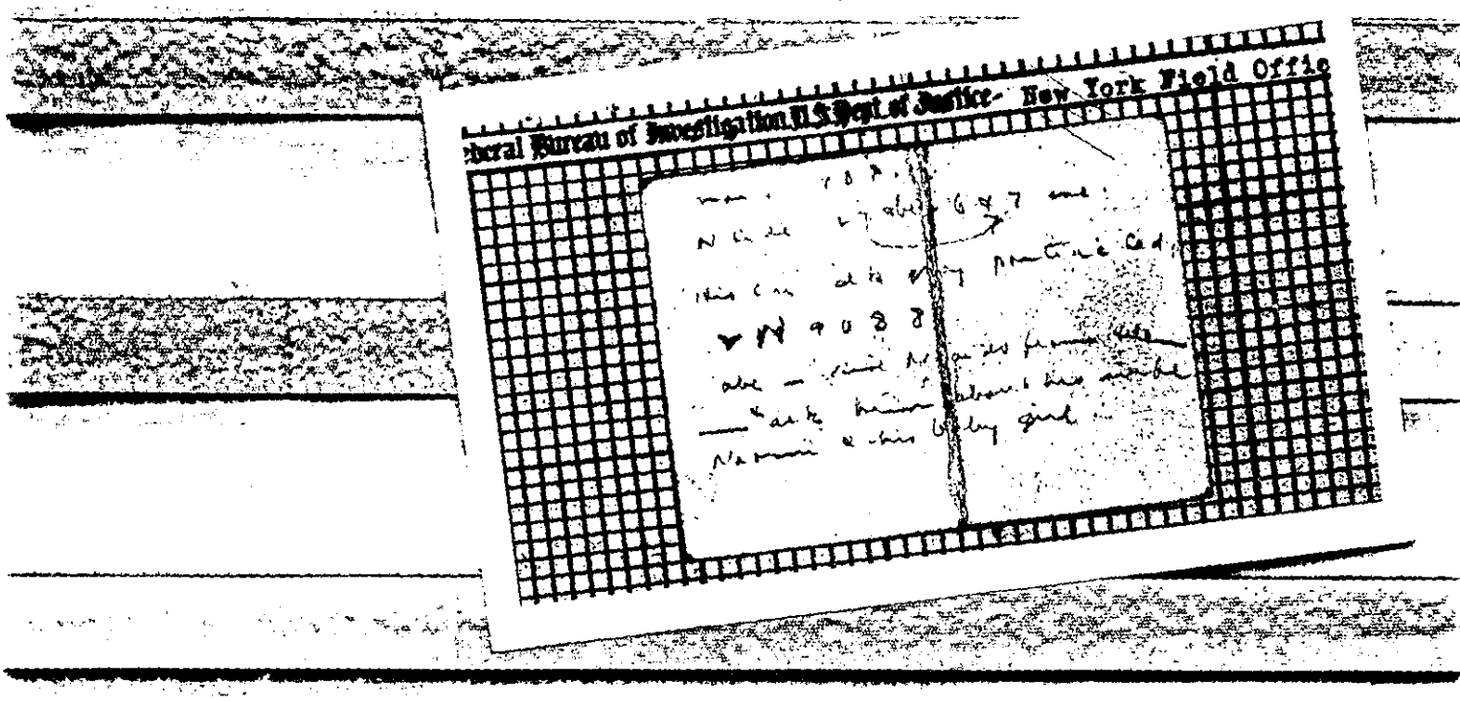
EXHIBIT NO. 65-4307-1-B-5 (29-10)

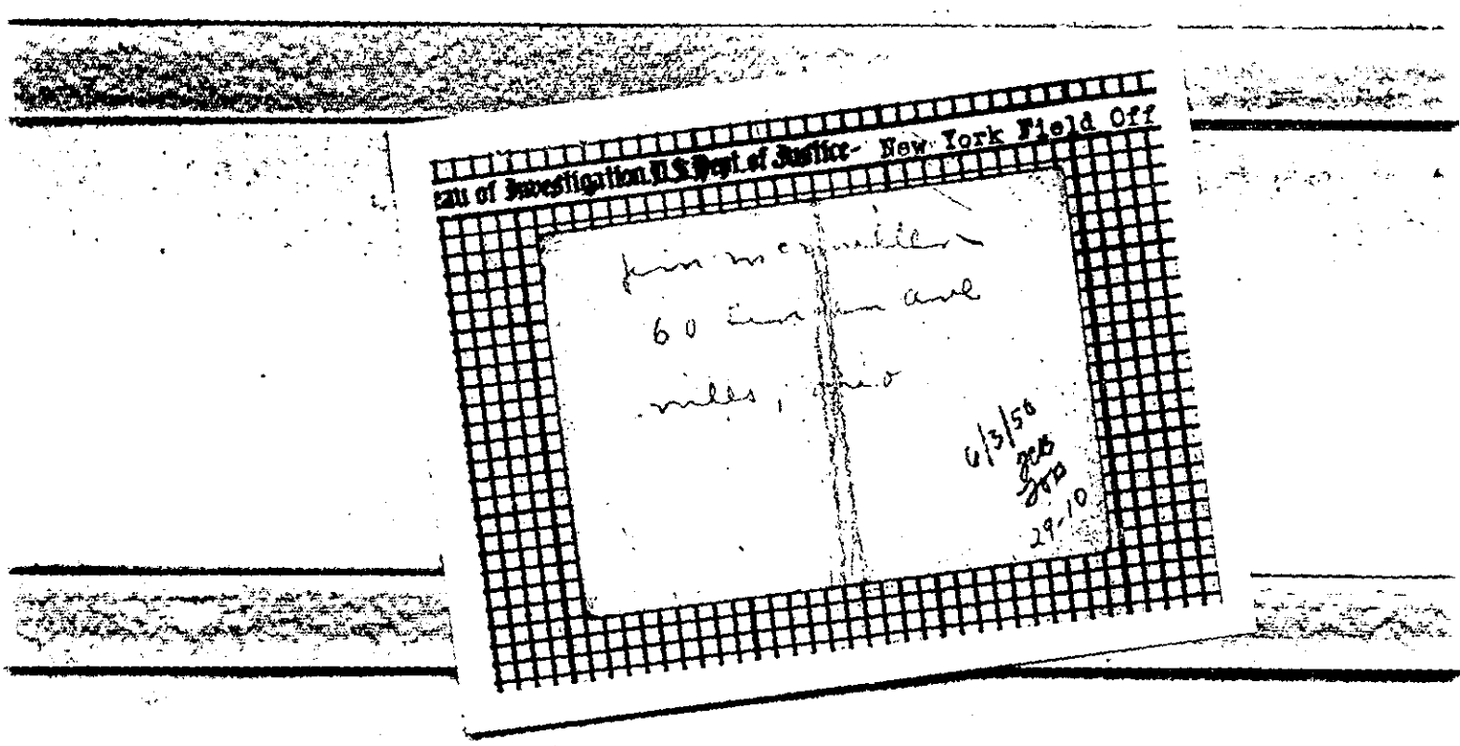
On 6/15/50, GOLD advised that the name appearing on this card was JIM McILVAIN, of 60 Lindon Avenue, Niles, Ohio. GOLD advised that McILVAIN attended Xavier University in Cincinnati while GOLD was in attendance there, and that McILVAIN played on the Xavier University football team. He was not in the same class as GOLD but was behind him in school. GOLD could not recall when he jotted this name down but stated that McILVAIN had no connection whatever with GOLD's espionage activities.

However, on the reverse side of this card appear some notations which GOLD stated were in his handwriting and which pertain to his espionage activity. GOLD said that these notations were jotted down when his Soviet superior, SAX, was giving him instructions upon GOLD's first contemplated contact with BROTHMAN on 9/29/41. GOLD stated that the entire message, without abbreviations, should read: "Monday, 10 p.m., north side of 27th Street between 6th and 7th Avenues, nearer 7th Avenue. His car (ABRAHAM BROTHMAN's) would be a dark gray Pontiac sedan bearing tags 219088." GOLD was to give the opening passwords as "Give regards from HARRY and ask him about his wife, HELEN, and his baby girl." GOLD stated he could not recall what BROTHMAN's answering password would be.

TSM:HEF
65-4307

The original of this card was introduced into evidence by The Government at Brotheman's trial and is being maintained by USA, SDNY


Federal Bureau of Investigation U.S. Dept of Justice- New York Field Office


Bureau of Investigation U.S. Dept of Justice- New York Field Off
6/3/50

SAC 6/27/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, WAS.
ESPIONAGE - R

65-4307-1-B-12 (4) - Folder #16

MATERIAL FOUND IN A WOODEN BOX IN THE BASEMENT OF GOLD'S HOME

This exhibit was shown to GOLD on 6/24/50 and consists of a manila folder containing three sheets of 8" x 11" white paper with handwriting thereon and two additional blank sheets of paper.

GOLD identified this as being in his handwriting and stated that the material was concerned with operating data on a magnesium powder plant. He said that this material had been given to him verbally by BROTHMAN in about the spring of 1943 for submission to the Soviet Union.

GOLD stated that the material had not been turned over to the Soviets because they were not interested in anything which was BROTHMAN's own design.

tsm/rac
65-4307

This material on magnesium powder was introduced in to evidence by The Government at Brothman's trial and is being maintained by USA, SDNY.

SAC 6/27/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, WAS.
ESPIONAGE - R

#3

65-4307-1-B-12 (3)

LOOSE PAGES OF MISCELLANEOUS PAPERS FOUND IN WOODEN BOX IN BASEMENT OF GOLD'S HOME

The above exhibit was shown to GOLD on 6/24/50 at which time he extracted various items which he stated dealt with the espionage activity of BROTHMAN and himself. These items are identified as follows:

(1) 11 pages of handwritten notes and handdrawn figures on legal size yellow paper which was admittedly in GOLD's handwriting. GOLD advised that this material was concerned with mixing equipment and that the material was verbally given to him by BROTHMAN for submission to the Soviet Union, probably sometime around July of 1942. GOLD stated he thought that this material was done on a Sunday morning in the offices of the Chemurgy Design Corporation.

(2) A 8" x 11" ruled yellow paper with the number 3 in the upper right hand corner and notations beginning "2. According to Trink . . . " GOLD said that this material was in BROTHMAN's handwriting and refers to the magnesium powder, and that this material had been given to GOLD by BROTHMAN for submission to the Soviet Union but GOLD did not turn such material over because the Soviets were not interested in it.

(3) An 8" x 11" piece of ruled yellow paper entitled "Notes on Computations". GOLD stated this was in his handwriting and refers to the magnesium powder and should go with #2 above.

(4) Four sheets of unruled white paper bearing the numbers, 16, 17, 18, and 19 in the upper right hand corners. GOLD stated that this was in his handwriting and the material refers to the Buna S Process. GOLD stated that the encircled numbers on the left hand side of the first two pages refer to the body of the

tam/rac
65-4307

Items 1, 3 + 4 above were introduced into evidence by the government at Brothman's trial and are being maintained by USN, SDNY

Buna S report--probably the preliminary report. GOLD stated that this material was given to GOLD by BROTHMAN for submission to the Soviets about February, 1942. GOLD stated that these notes are obviously explanations to a report previously given.

(5) A sheet of white 8" x 11" paper with the numeral 7 on top, and containing typewriting and handwriting. GOLD stated that this page contains his handwriting and that the material refers to mixing equipment. GOLD said that this was given to him by BROTHMAN for transmission to the Soviets and that he thought this material was typed in the offices of the Chemurgy Design Corporation. GOLD stated that he got a more complete report later from BROTHMAN on the mixing equipment during the late summer or early fall of 1942.

GOLD went through the remainder of the material in this folder and stated that it contained tutoring notes, notes and work at the Pennsylvania Sugar Company, drafts of letters to be used by GOLD and M. E. DOUGHERTY when they were considering doing vitamin assay work, and methods of vitamin assays.

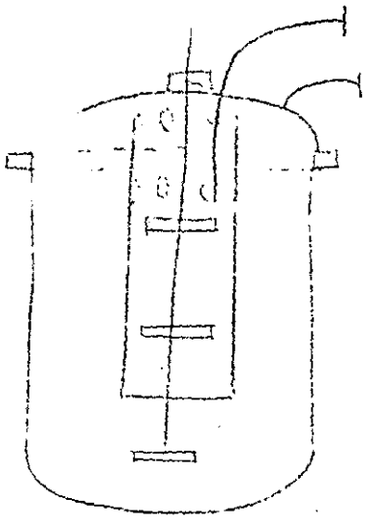
Also contained in this folder was a letter dated 12/1/42 to Mr. A. BROTHMAN, 420 Lexington Avenue, New York, N. Y. which was unsigned. GOLD identified this letter as dealing with the process of nickel recovery which was legitimate work he was doing for BROTHMAN at that time and for which he got paid. He said this had nothing to do with the Soviets.

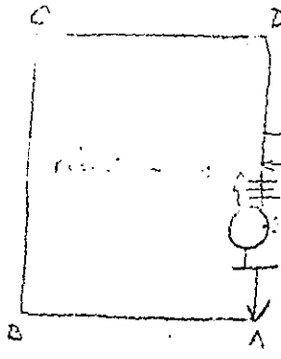
Also contained among these papers was a 12 page document entitled "A Vitamin Assay Laboratory". GOLD advised that this document was drawn up by GOLD and DOUGHERTY when they were seeking a loan from the Corn Exchange Bank in Philadelphia, Pa. in the amount of $1,400, with which they were going to start their Vitamin Assay business. GOLD said that this attempt to secure a loan from the Corn Exchange was unsuccessful. GOLD pointed out that there were four people interested in the proposed company. Other than DOUGHERTY and GOLD, the individuals were DR. FRANCES EDEL and OTTO H. SIEBERT.

GOLD said that DR. EDEL was a woman who worked at National Oil Products Corporation (NOPCO) and who had been introduced to GOLD and DOUGHERTY by THOMAS L. BLACK. The other individual, OTTO H. SIEBERT, was a partner in the firm TERRY & SIEBERT which was an established chemical laboratory and which name the company was going to use on their letterhead in attempting to secure business in the vitamin assay field.

GOLD stated that it was probably late 1941 or January of 1942 that they were attempting to secure the money to start the laboratory.

Also contained among these papers were various newspaper clippings which referred to vitamin data.





$$C = f(t)$$

If $P_1 + P_2 + P_3 + \dots P_n = 1$
and if $(\bar{C})$ is to [illegible] the mean
[illegible]

then

$$P_1 [f(t_1)] + P_2 [f(t_2)] + P_3 [f(t_3)] + \dots P_n [f(t_n)]$$
$$= (\bar{C})$$

Let us [illegible] the values of
$P_1, P_2, P_3 \dots P_n$ from Fig A

The probability of a particle entering the system at R & being [illegible] at time [illegible]

1) The probability of [illegible] $\frac{R}{Q} = p$
2) The [illegible] $(1-p)p$
3) The probability [illegible] $(1 - \{p + (1-p)p\})p$
4) The probability [illegible]
$$= \{1 - (p + (1-p)p + [1 - \{p + (1-p)p\}]p)\} p$$

6/6/5[illegible]

Let us simplify (3)

$$(1 - p - p + p^2)\, p = (1 - 2p + p^2)\, p$$
$$= (1 - p)^2\, p$$

Let us simplify (4)

$$(1 - p - p + p^2 - p + p^2 + p^2 - p^3)\, p$$

$$= (1 - 3p + 3p^2 - p^3)\, p$$

$$= (1 - p)^3\, p$$

Let $(1 - p) = q$

Then it will be seen that we may write in Fig B

Let us consider 2 machines in [illegible] (series):-

The probability for a sequence of 2 passes (i.e., 1 pass in each machine) would equal p^2

The probability for a sequence of 3 passes in such a sequence (i.e., 1 pass in machine and 2 in the other) would be $(p - p^2 + pq)\, p = \{(1-p)p + pq\}\, p$

$$= (pq + pq)\, p = 2p^2 q$$

The probability of a sequence of 4 passes in two machines would be

$$d\left(\frac{1}{2}b^2 + \frac{1}{2}b^2 - bd + \frac{1}{2}d^2 - d\right)$$

$$= d\left(\frac{1}{2}b^2 + \frac{1}{2}d^2 - bd - d\right)$$

$$= d\left(\frac{1}{2}b^2 + \frac{1}{2}d^2 - bd - 2d\right)$$

$$= d\left(\frac{1}{2}b^2 + \frac{1}{2}d^2 - bd - 4d + 2d\right)$$

$$= d\left(\frac{1}{2}(b-d)^2 - 4d + 2d\right)$$

$$= d\left(\frac{1}{2}(b-d)^2 - 2(2d) + 2d\right)$$

$$= d\left(\frac{1}{2}(b-d)^2 - 2(2d) + 2(2)\right)$$

$$= d\left(\frac{1}{2}(b-d)^2 - 2(2d-2)\right)$$

$$= d\left(\frac{1}{2}(b-d)^2 - 2(d-1)\right)$$

$$= d\left(\frac{1}{2}(b-d)^2 - 2(d-1)\right)$$

$$= \frac{1}{2}d(b-d)^2 - 2d(d-1)$$

$$= \frac{1}{2}d(b-d)^2 - 2d^2 + 2d

6/6/50
JP

The probability of 5 passes in 4 machines

$$= (p^3 - p^4 + 3p^3q)\,p$$

$$= (1 - p + 3q)\,p^4$$

$$= 4qp^4 = 4p^4q$$

The probability of 6 passes in 4 machines

$$= (p^3 - p^4 + 3p^3q - 4p^4q + 6p^3q^2)\,p$$

$$= (1 - p + 3q - 4pq + 6q^2)\,p^4$$

$$= (q + 3q - 4(1-q)q + 6q^2)\,p^4$$

$$= (q + 3q - 4q + 4q^2 + 6q^2)\,p^4$$

$$= (10q^2)\,p^4 = 10p^4q^2$$

Fig 1 [illegible] [illegible] demonstration of a Pascal Δ

$$\binom{n-1}{k-1} p^k q^{n-k}$$

Consider a [illegible] reaction

The integrated form of the [illegible] [illegible] will be

$$t = \frac{2.303}{k_1} \log \frac{a}{a-x}$$

Let $\frac{1}{k_1} = \lambda_1^{-1}$

Let $t = n t_m$

Thus

t is stated in terms of multiples (n) of the minimum time t_m

So, $\log_e \frac{a}{a-x} = \lambda_1 n t_m$

or $\frac{a}{a-x} = e^{\lambda_1 n t_m}$

[illegible]

6/6/[illegible]

C[illegible] Third order reaction :-

The integrated form of the reaction velocity equation is :-

$$(1)\quad t = \frac{2.303}{k_3}\left[\frac{1}{a'c'}\log\frac{a}{a-v} + \frac{1}{a'b'}\log\frac{b}{b-v} + \frac{1}{b'c'}\log\frac{c}{c-v}\right]$$

where

$$a' = (a-b),\quad b' = (b-c),\ \&\ c' = (c-a)$$

Let $\frac{1}{k_3} = \lambda_3^{-1}$

Let $t = n\,t_m$

Log A + Log B = Log (AB)

Rewriting (1)

$$t = \frac{2.303}{k_3}\log\left[\left(\frac{a}{a-v}\right)^{\frac{1}{a'c'}}\left(\frac{b}{b-v}\right)^{\frac{1}{a'b'}}\left(\frac{c}{c-v}\right)^{\frac{1}{b'c'}}\right]$$

or as before

$$\overbrace{\left[\left(\frac{a}{a-v}\right)^{\frac{1}{a'c'}}\left(\frac{b}{b-v}\right)^{\frac{1}{a'b'}}\left(\frac{c}{c-v}\right)^{\frac{1}{b'c'}}\right]}^{P} = \overbrace{e^{\lambda_3 n t_m}}^{f(t)}$$

or as in the preceding two cases

$$\overline{\left[\left(\frac{a}{a-v}\right)^{\frac{1}{a'c'}}\left(\frac{b}{b-v}\right)^{\frac{1}{a'b'}}\left(\frac{c}{c-v}\right)^{\frac{1}{b'c'}}\right]}$$

$$= \sum_{n=k}^{\infty}\binom{n-1}{k-1}p^k q^{n-k} e^{\lambda_3 n t_m}$$

2. for the flange load H_t

$$(5,150)(1.125) = 5800 \text{ lbs.}$$

3. for the flange load H_g

$$(17,700)(0.875) = 15,500 \text{ lbs.}$$

The total moment acting the flange would be

$$\begin{array}{r} 5,800 \\ 15,500 \\ 48,800 \\ \hline 70,100 \end{array} \text{ inch-lbs.}$$

while the unit moment would be

$$\frac{70,100}{24} = 2920 \text{ lbs.}$$

where 24" is the inside diameter of the flange.

For a ratio of flange O.D. to flange I.D. of

$$\frac{28.375}{24} = 1.18$$

the Taylor-Waters factor would be 12.0

and the minimum flange thickness required

$$\left[\frac{(2920)(12)}{14,000}\right]^{\frac{1}{2}} = 1.58"$$

Assuming equal distribution of the flange moment, taking the Code Approved stress for an ASTM forged steel material (ASTM-181) to be 14,000 psi, the Taylor-Waters factor as above, and the unit moment in the flange as calculated above. The correction factor for uneven distribution of flange moment may be estimated by the equation

$$\left(\frac{k}{2z+t}\right)^{\frac{1}{4}} = \left(\frac{3.65}{(1.5+1.58)}\right)^{\frac{1}{4}} = 1.04 \qquad \frac{\pi(2.75)}{3} = k = 3$$

where k is the distance between bolts, z the diameter of the bolts used and t the thickness of flange as arrived at above. The final adopted flange thickness was then taken to be

$$(1.58)(1.04) = 1.64", \quad 1\tfrac{5}{8}"$$

Proceeding to the design of the agitator assembly, actually used in view of conservative design stress for flange, it was decided to use an assembly consisting of two turbines for the following reasons. In normal practice for vessels whose diameters exceed 36" or whose holding capacities exceed 200-gallons, the diameter of turbine rotors used runs from 1/3 to 1/4 the diameter of the containing vessel. In order to reduce the angular velocity of the agitator shaft to a minimum, the upper part of the rotor diameter-to-kettle diameter range was employed, and hence a

$$\frac{36}{3} = 12" \text{ diameter rotor}$$

was nominated. In order to confine the turbine rotor speed below

PENNSYLVANIA SUGAR COMPANY

INTER-OFFICE CORRESPONDENCE

10/20/36

October 20, 1936.

Mr. W. H. Hoodless, Vice-President
Refinery.

Dear Sir:

The results of analysis of the syrups submitted on October 14, 1936 are as follows:

Analysis	Penn Mar Golden Syrup - at 27¢ lb. Sugar	Duff's New Orleans Molasses at $1.39 per gal.
% Solids	78.30	79.20
% Sucrose	36.25	44.60
% Invert	37.65	18.73
% Combined Sugars	73.90	63.33
% Ash	0.35	5.50
pH	5.42	6.18

Very truly yours,

Harry Gold

Chemical Department

HG:CH

CC: DR. G. T. REICH

(5)

6/6/50
RB

(5) $\cos x \cdot \csc x = \cot x$

$\cos x \dfrac{1}{\sin x} = \cot x$

$\dfrac{\cos x}{\sin x} = \cot x$

$\cot x = \cot x$ [illegible]

---

(3) $\dfrac{\sin x}{\cos x} + \dfrac{\cos x}{\sin x} = \csc x$

$\dfrac{\sin^2 x + \cos^2 x}{\cos x \sin x} = \csc x \sec x$

$\dfrac{1}{\cos x \sin x} = \csc x \sec x$

$\csc x \sec x = \csc x \sec x$

---

(4) $\dfrac{\sin x}{1+\cos x} + \dfrac{1+\cos x}{\sin x} = 2\csc x$ $\quad$ [illegible]

$\dfrac{\sin^2 x + 1 + 2\cos x + \cos^2 x}{(1+\cos x)(\sin x)} = 2\csc x$

$\dfrac{\cancel{\sin^2 x + \cos^2 x} + 1 + 2\cos x}{(1+\cos x)(\sin x)} = 2\csc x$ $\quad$ [illegible]

$$\frac{2 + 2\cos v}{(1+\cos v)(\sin v)} = 2\csc v$$

$$\frac{2\cancel{(1+\cos v)}}{\cancel{(1+\cos v)}(\sin v)} = 2\csc v$$

$$\frac{2}{\sin v} = 2\csc v$$

$$2\csc v = 2\csc v$$

Error

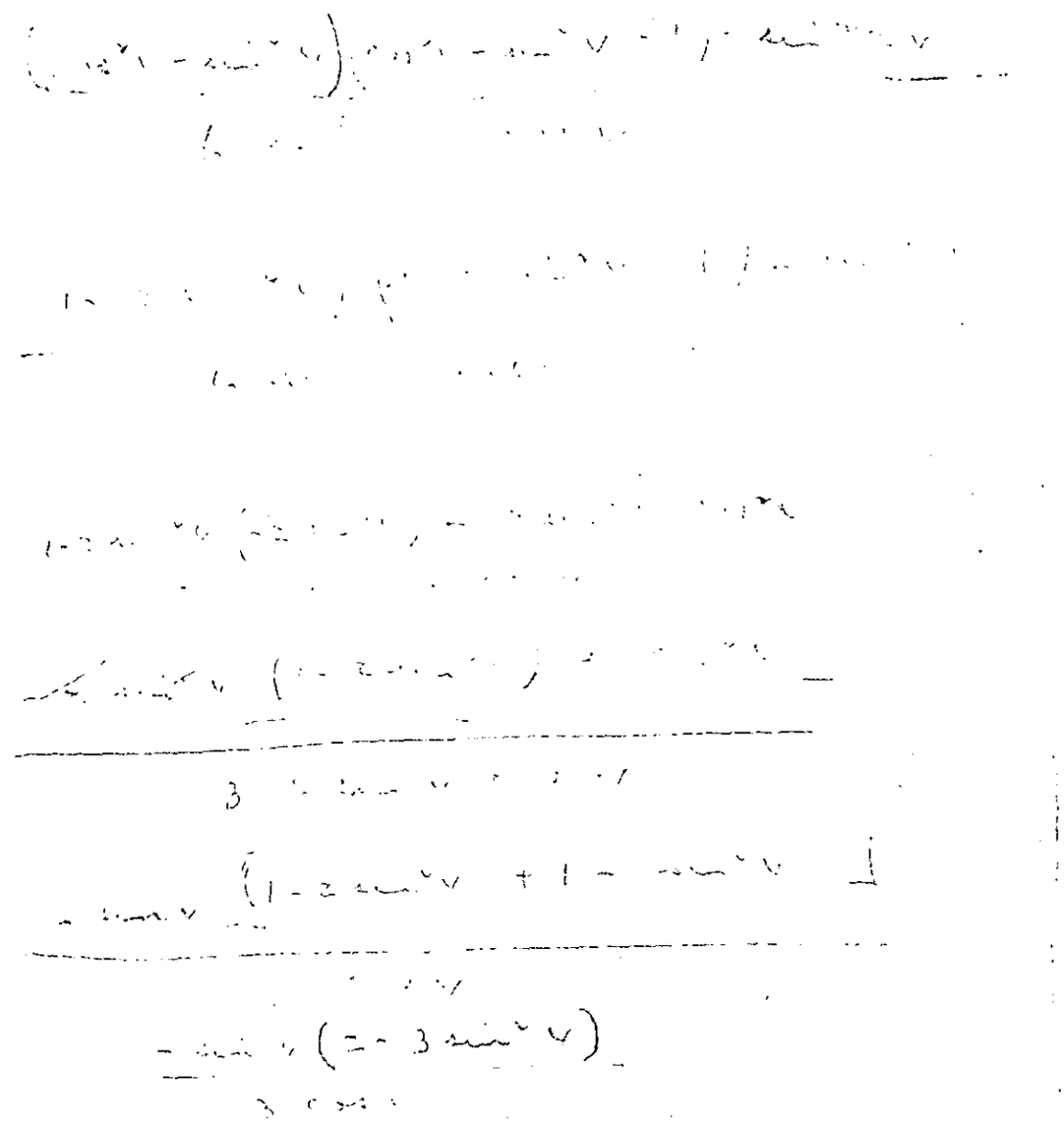
$$\frac{\left(\cos^2 v - \sin^2 v\right)\left(\cos^2 v - \sin^2 v - 1\right) - \sin^2 v}{\ldots}$$

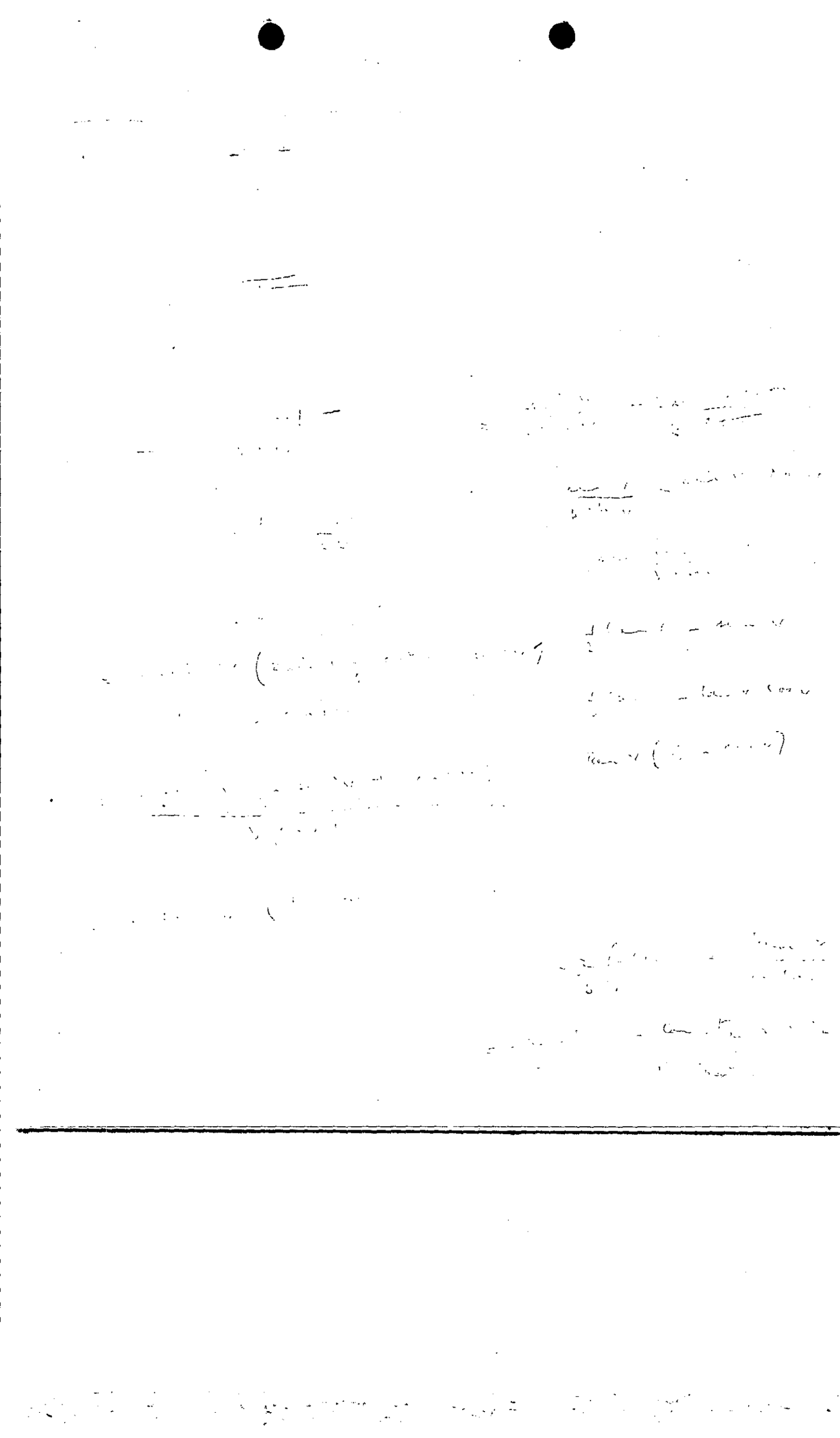
$$\frac{\ldots}{\ldots}$$

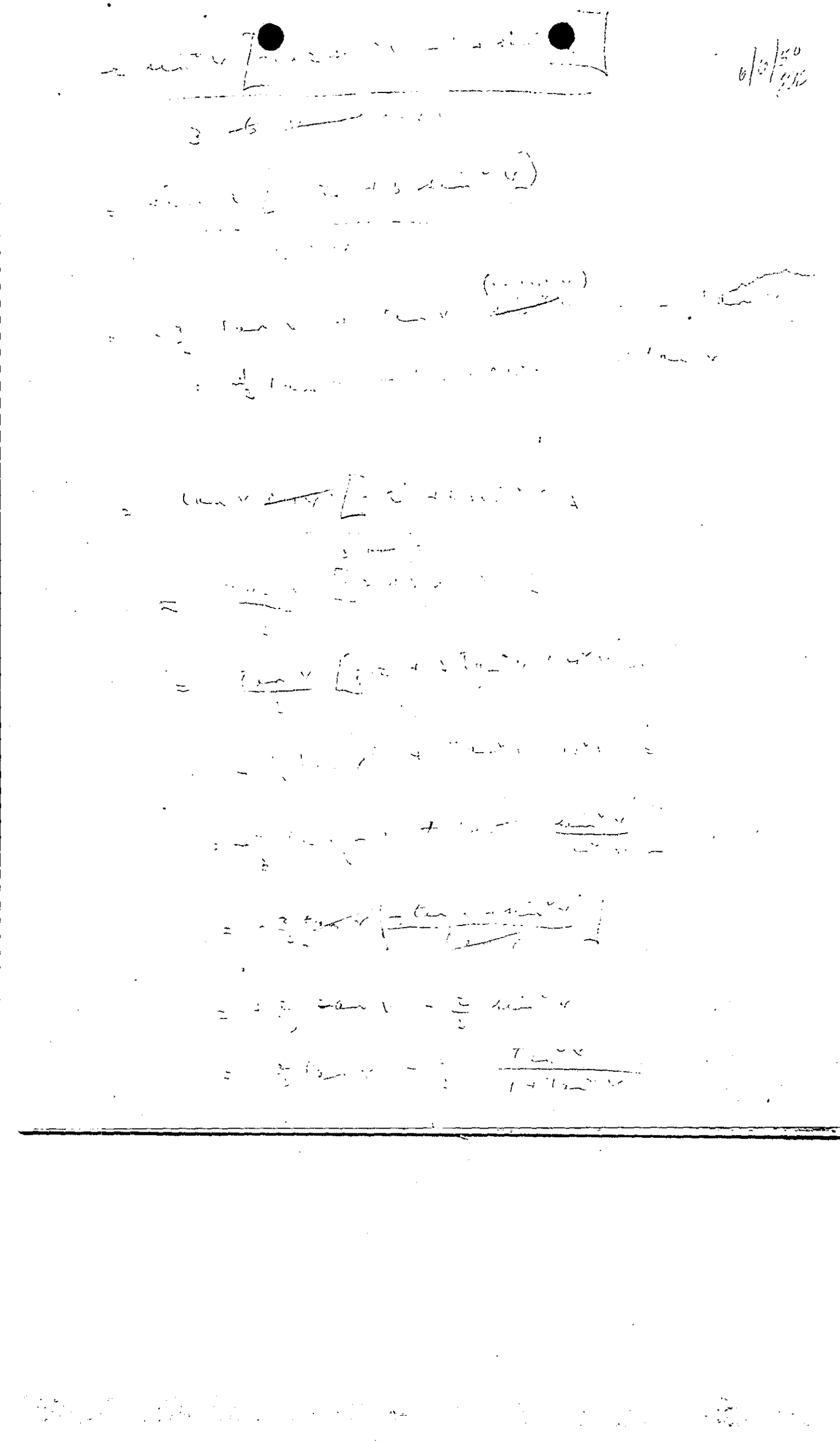
$$\frac{\ldots\left(1 - 2\sin^2 v\right) \ldots}{3 \ldots}$$

$$= \frac{\ldots \sin v \left(1 - 2\sin^2 v + 1 - \sin^2 v\right)}{\ldots}$$

$$= \frac{-\sin v\left(2 - 3\sin^2 v\right)}{3 \cos \ldots}$$







3/19/41

Flue Gas Analysis

0.247 SO_3

$1 \times 9.5^2 \times 0.785 = 70.9''^2$

231

0.0411 ft^3 = 0.307 gal/"

× 11" = ~~3.38 gal~~

3.48

3.46

$\frac{62}{128}$

2×10^{-4}

12×10^{-3}

~~0.0117~~ | 2.2×10^4

~~64.06~~

6.4×10

0.012 am SO_2

4

0.003 × 3

4.2×10^2

$\frac{4924}{17500}$ × ~~10~~

0.7×10^4

0.0243

0.

11" / [illegible]

[illegible]

150 ml. I_v

15 inches total / 1 hr. 44 min

10 °C

137.73

134.06 of 1.000 N $Na_2S_2O_3$ compl.

3.67 ml. N I_v

45.91 I_v

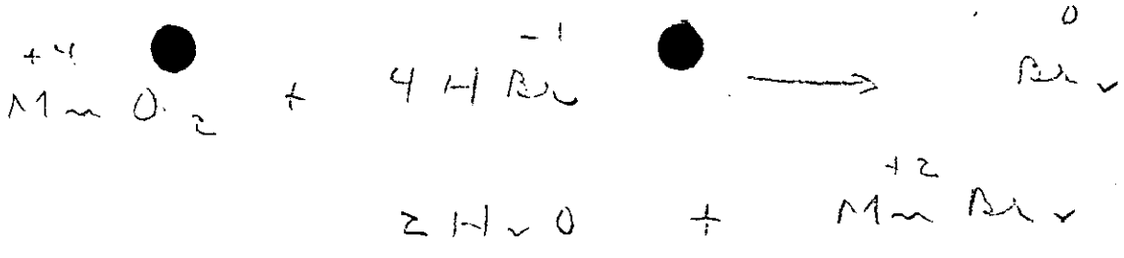
3

137.73

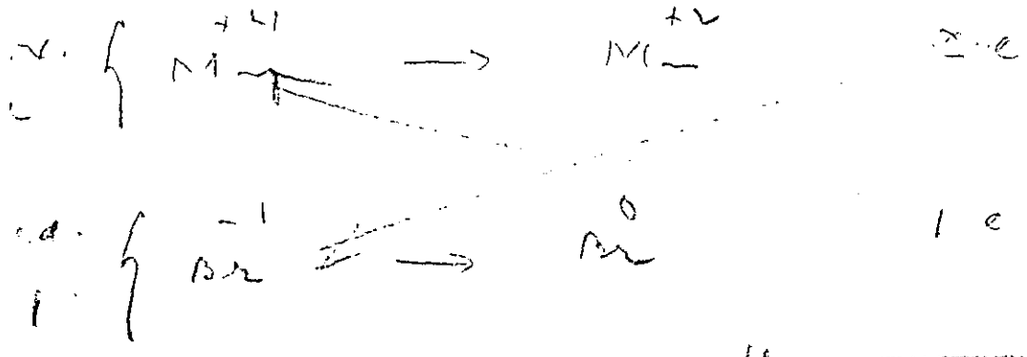
3.67 × 0.1000 × 0.03203 = 0.01174 gm. SO_2

1167 cc / "

1167 × 15 = 17500 cc.



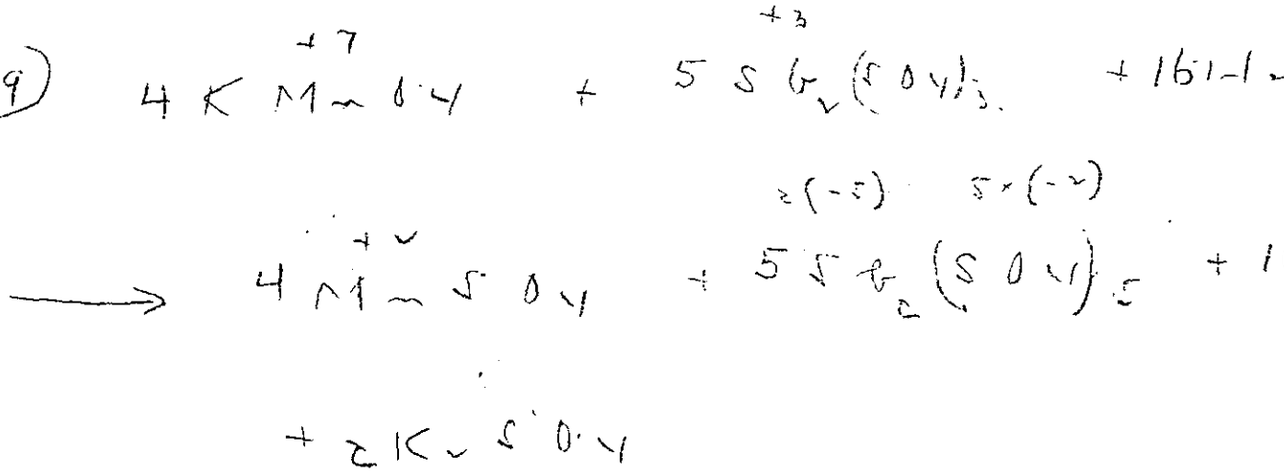
(93) $\overset{+4}{Mn}O_2 + 4H\overset{-1}{Br} \longrightarrow \overset{0}{Br_2}$



$2H_2O + \overset{+2}{Mn}Br_2$

ox. $\{ \overset{+4}{Mn} \longrightarrow \overset{+2}{Mn}$ 2 e

red. $\{ \overset{-1}{Br} \longrightarrow \overset{0}{Br}$ 1 e



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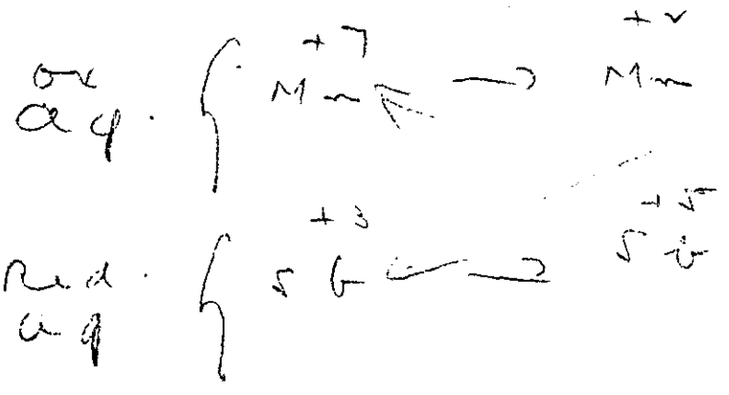
(89) $4K\overset{+7}{Mn}O_4 + 5\overset{+3}{Sb_2}(SO_4)_3 + 16H_2S$

$2(-5) \quad 5\times(-2)$

$\longrightarrow 4\overset{+2}{Mn}SO_4 + 5Sb_2(SO_4)_5 + 16$

$+ 2K_2SO_4$



ox aq. $\{ \overset{+7}{Mn} \longrightarrow \overset{+2}{Mn}$ 5 e

Red. aq $\{ \overset{+3}{Sb} \longrightarrow \overset{+5}{Sb}$ 2 e

---

6/6/50

(1) $2S + 2O_2 \xrightarrow{\Delta} 2SO_2$

Then

$2SO_2 + O_2 \xrightarrow[Pt]{} 2SO_3$

---

(2) $2Al + 3S \xrightarrow{\Delta} Al_2S_3$

---

(3) $Mg + Pb(NO_3)_2 \longrightarrow Mg(NO_3) + Pb$

---

(4) $2\overset{0}{Al} + 3\overset{0}{Br_2} \longrightarrow 2\overset{+3}{Al}\overset{-1}{Br_3}$

Red eq $\{ \overset{0}{Br} \longrightarrow \overset{-1}{Br}$ 1e

Red eq $\{ \overset{0}{Al} \longrightarrow \overset{+3}{Al}$ 3e

---

(6) $2\overset{0}{Si} + \overset{+1}{K}\overset{-2}{O}\overset{+1}{H} + 2H_2O \longrightarrow$

$2K_2\overset{+4}{Si}O_3 + 4\overset{0}{H_2}$

ox aq $\overset{+1}{H} \rightarrow \overset{0}{H}$ 1 e

red $\overset{0}{Si} \rightarrow \overset{+4}{Si}$ 4 e

(7) $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$

(8) $\overset{+2}{Fe}O + \overset{0}{H_2} \longrightarrow \overset{0}{Fe} + H_2O$

ox aq $\overset{+2}{Fe} \rightarrow \overset{0}{Fe}$ 2 e

red aq $\overset{0}{H} \rightarrow \overset{-1}{H}$ 1 e

(9) $2HNO_3 + Ca(OH)_2 \longrightarrow$

$Ca(NO_3)_2 + 2H_2O$

(79.)

$\overset{+2}{K_2}\overset{+6}{Cr_2}\overset{(-)}{O_7}\overset{-14}{}$ + $14\overset{+1}{H}Cl$ ⟶

oxidizing agent reducing agent

$Cr_{+6} \longrightarrow Cr_{+3}$

$- \longrightarrow +$

$Cl_{-1} \longrightarrow Cl_{0}$

$3\overset{0}{Cl_2} + 2KCl + 2\overset{+3}{Cr}$

$+ 7H_2O$

6 HCl for Cl

2 HCl for K

2 HCl for Cl

10 HCl

8 Cl

6 Cl

(59) $\overset{+1}{K}\overset{+7}{Mn}\overset{-8}{O_4} + \overset{+3}{As}\overset{-3}{Cl_3} + H_2SO_4$

$\longrightarrow 2K_2SO_4 + \overset{+2}{Mn}SO_4 +$

$+ As_2(SO_4)_3 + 16H_2O + 15$

$Mn_{+7} \longrightarrow Mn_{+2}$ — 5

$Cl_{-1} \longrightarrow Cl_0$ 1 6 8

(59) $2KM^{+}_{-}O_4 + 5As^{+3}Cl_3^{-} + 8H_2SO$

$\longrightarrow 2KCl + 2M^{+2}_{-}SO_4 + 2As^{+3}_{2}S$

$+ 4Cl^{0}_{2} + As^{+5}Cl_5 + 8H$

$\left\{ \begin{array}{l} Mn \longrightarrow Mn \quad 5 \\ +4 \quad\quad +2 \end{array} \right.$

$\left\{ \begin{array}{l} Cl \longrightarrow Cl \\ -1 \quad\quad 0 \\ As \longrightarrow As \quad 2 \\ +3 \quad\quad +5 \end{array} \right.$

(54) $2Sb^{+5}Cl_5^{-5} + Pb^{+4}O_2 + 4H_2SO_4$

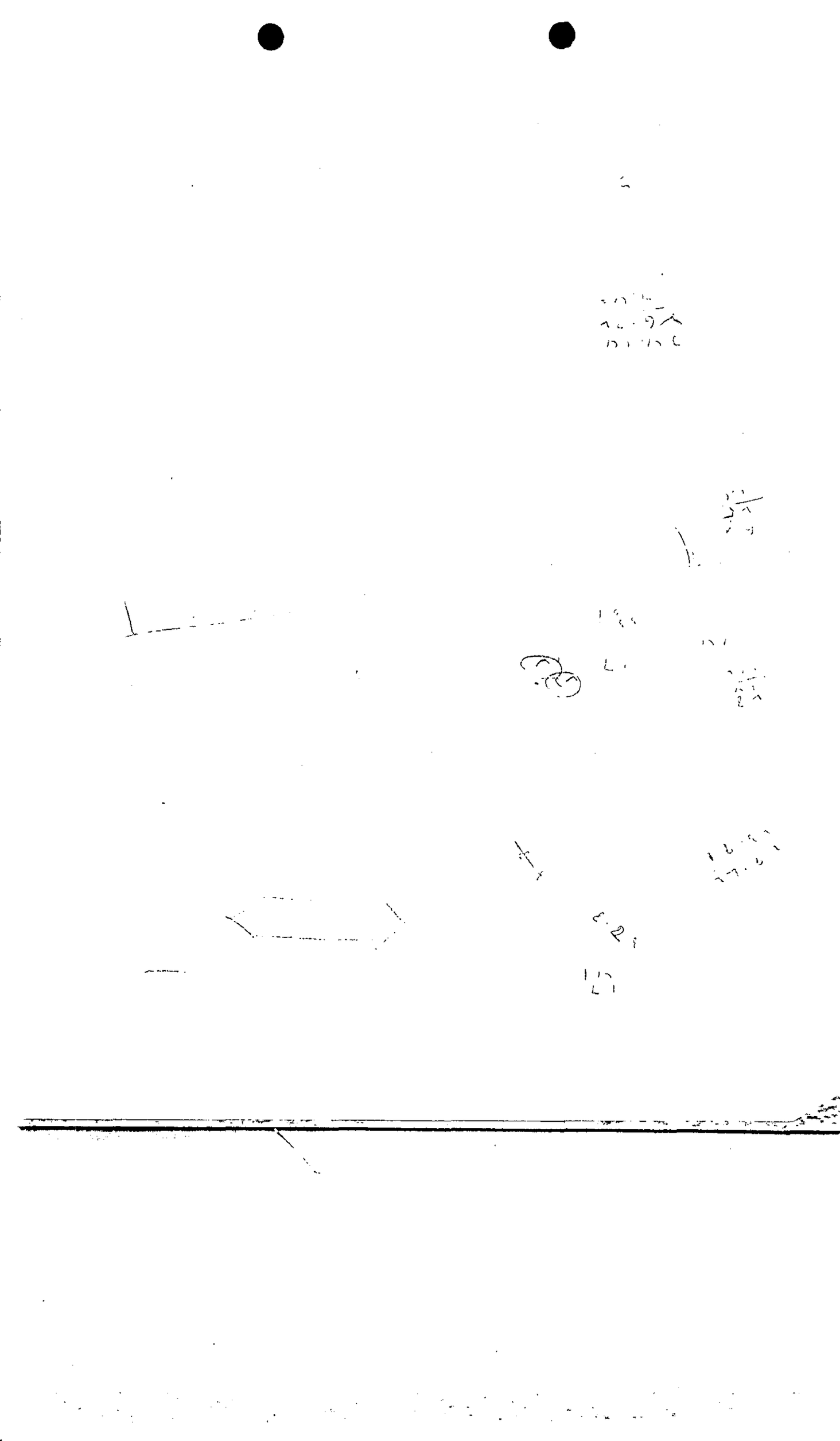
$\longrightarrow Sb_2(SO_4)_3 + 3Cl^{0}_{2} + Pb$

$(+3)\times 2 \quad (-2)\times 3$

$4HCl + 2H$

$\left\{ \begin{array}{l} Pb \longrightarrow Pb \quad 2 \\ +4 \quad\quad +2 \\ Sb \longrightarrow Sb \quad 2 \\ +5 \quad\quad +3 \end{array} \right.$

red. eq. $\left\{ \begin{array}{l} Cl \longrightarrow Cl \quad 1 \\ -1 \quad\quad 0 \end{array} \right.$



$2FeCl_3 + SnCl_3 \longrightarrow 2FeCl + SnCl_5$

ox aq $Fe^{+3} \longrightarrow Fe^{+2} + 1e$

Red aq $Sn^{+3} \longrightarrow Sn^{+5} + 2e$

$2Fe_3(PO_4)_2 + K_2Cr_2O_7 + 5H_3PO_4$

$\longrightarrow K_2HPO_4 + 6FePO_4 + 2CrPO_4 + 7H_2O$

ox aq $Cr^{+6} \longrightarrow Cr^{+3} + 3e$

Red aq $Fe^{+2} \longrightarrow Fe^{+3} + 1e$

KH_2PO_4

K_2HPO_4

K_3PO_4

(91) $Cu^{0} + 4HN^{+5}O_3$ (dil) $\longrightarrow Cu(NO$

$+ 2H_2O + 2N^{+4}O_2$

Ox. aq. $N^{+5} \rightarrow N^{+4} + 1e$

Red. aq. $Cu^{0} \rightleftharpoons Cu^{+1} + 2e$

---

(92) $3Cu + 8HNO_3$ (conc.) $\longrightarrow 3Cu(N$

$4H_2O + 2N$

Ox. aq. $N^{+5} \rightarrow N^{+4} + 3e$

Red. aq. $Cu^{0} \rightarrow Cu^{+2} + 2e$

---

(80) $Ba(NO_3)_2 + K_2(Cr_2O_7)^{+6}$ ——

$BaCr_2O_7 + 2KNO_3$

---

(33) $2KOH + CO_2 \longrightarrow K_2CO$

$+ H_2O$

$KOH + CO_2 \rightarrow KHCO$

and,

$KHCO_3 + KOH \rightarrow K_2CO_3$

$+ H_2O$

---

(51) $4HCl^{-1} + \overset{0}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + 2\overset{0}{Cl}_2$

ox aq $\overset{0}{O} \rightarrow \overset{-2}{O}$ 2 e

red $Cl^{-1} \leftarrow \overset{0}{Cl}$ 1 e

---

(53) $\overset{0}{Cl}_2 + H_2O \longrightarrow HCl^{-1} +$

$\overset{+1}{H}\overset{+1}{Cl}\overset{-2}{O}$

ox aq $\overset{0}{Cl} \rightarrow \overset{-1}{Cl}$

red aq $\overset{0}{Cl} - \overset{+1}{Cl}$

$$2\,K\overset{+7}{Mn}O_4 + 5\,H_2\overset{+3}{C_2}O_4 + 3\,H_2SO_4 \longrightarrow 10\,\overset{+4}{C}O_2 + 2\,\overset{+2}{Mn}SO_4 + K_2SO_4 + 8\,H_2O$$

ox. aq: $\overset{+7}{Mn} \rightarrow \overset{+2}{Mn}$ 5 e

red. aq: $\overset{+3}{C} \rightarrow \overset{+4}{C}$ 1 e

$$S^0 + 4\,H\overset{+5}{N}O_3 \longrightarrow \overset{+4}{N}O_2 + \overset{+4}{S}O_2 + 2H_2O$$

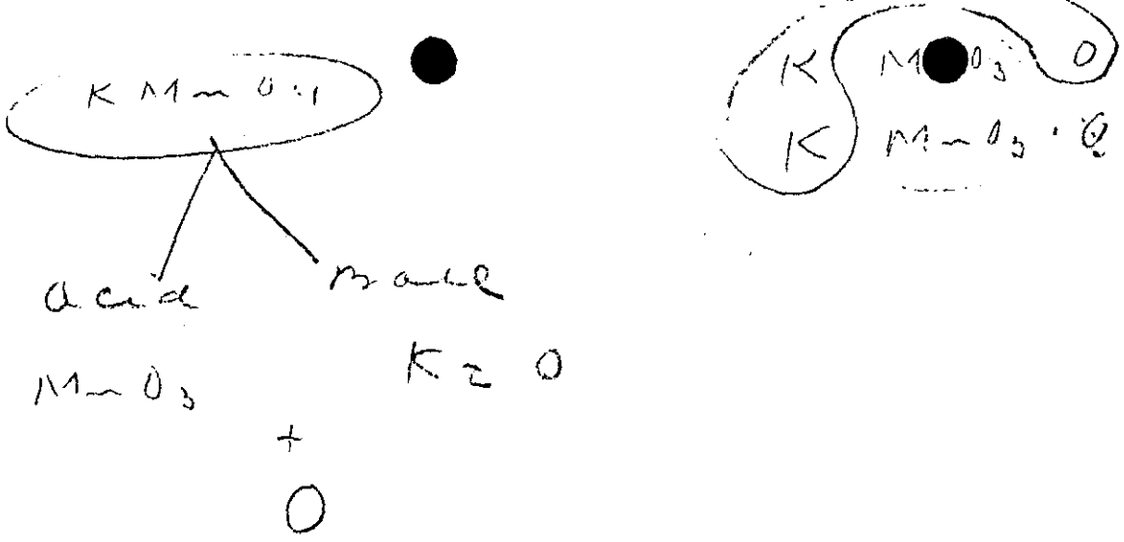
ox. aq: $\overset{+5}{N} \rightarrow \overset{+4}{N}$ + 1 e

red. aq: $S^0 \rightarrow \overset{+4}{S}$ − 4 e

$$S^0 + 6\,H\overset{+5}{N}O_3 \longrightarrow 6\,\overset{+4}{N}O_2 + \overset{+6}{S}O_3 + 3H_2O$$

ox. aq: $\overset{+5}{N} \rightarrow \overset{+4}{N}$ 1 e

red. aq: $\overset{0}{S} \rightarrow \overset{+6}{S}$ 6 e



$K_2Cr_2O_7 \rightarrow (K_2CrO_3 \cdot CrO_3 \cdot O)$

$HNO_3 \rightarrow (H \cdot NO_3 \cdot O \;\; H \cdot NO_2 \cdot O)$

Conc $HNO_3 \rightarrow$ (NO_2 or N_2O_4)

Dil $HNO_3 \rightarrow$ N_2 or N_2O

(49) $2Pb(\bullet)_2 \xrightarrow{\Delta} 2P\bullet O + O_2$

Decomposition

---

(60) $2K_2\overset{+6}{Cr}O_4 + 6\overset{+2}{Fe}SO_4 + 8H_2SO_4$

$\longrightarrow 2K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 3\overset{+3}{Fe_2}(SO_4)_3 + 8H_2O$

Ox aq $\overset{+6}{Cr} \rightarrow \overset{+3}{Cr}$ 3e

Red aq $\overset{+2}{Fe} \rightarrow \overset{+3}{Fe}$ 1e

---

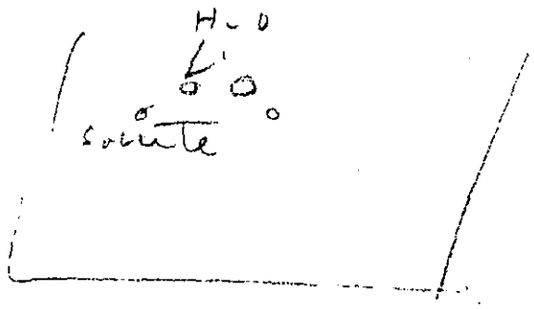
(90) ?

$NaCrO_2 + ZnCl_2 + H_2SO_4$

$\longrightarrow ZnCr_2O_7 + 2NaCl + H_2SO_4$

Colloids Ch. 10

True Soln vs Colloidal Dispersion

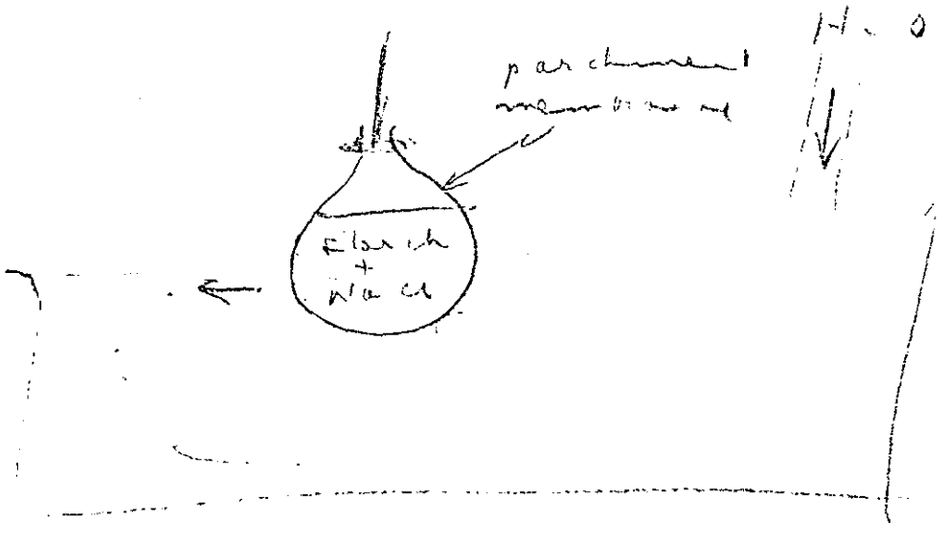


Emulsion - whatever

Tyndall Effect

Brownian movement

Dialysis



Ch. 11

Gay-Lussac's Law

$3\,H_2 + N_2 \rightarrow 2\,NH_3$

3 vols 1 vols 2 vols

$2\,H_2 + O_2 \rightarrow 2\,H_2O$

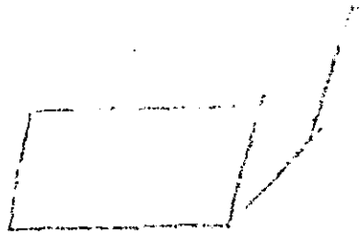
2 vols 1 vol 2 vols. Steam

Avogadro's Law

→ G.M.V. = 22.4 lit

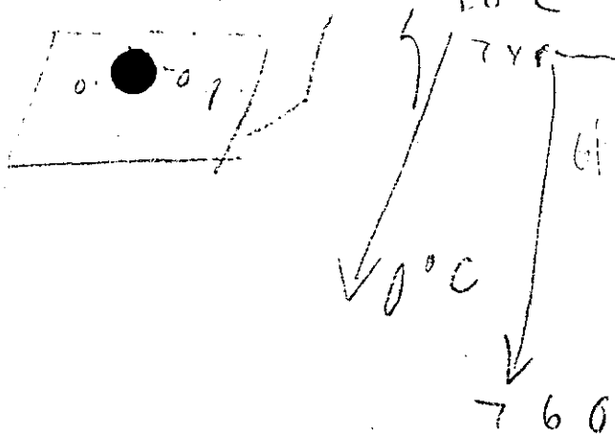
= 6.06×10^{23} molecules / G.M.V.

G.M.V.



(9)
p. 19 v

Vol at S.C.



$$110 \times \frac{273}{293} \times \frac{745}{760}$$

$= 100.4$ c.c. Vol at S.C.

1 liter of gas

$$\frac{1000}{100.4} \times 0.250 = 2.51 \text{ gms/liter at S.C.}$$

~~1.293 g air~~

~~$\frac{2.51}{1.293} \times 2$~~

$$\begin{array}{r} 1.201 \\ \times 1.293 \\ \hline \end{array}$$

$2.51 \times 22.4 = 56.3$

~~0.1004~~

$$\frac{100.4}{22,400} \qquad \frac{22,400}{100.4} \times 0.250 =$$

$\overset{+4}{Mn}O_2 + 4HCl^{-1} \rightarrow \overset{0}{Cl_2} + \overset{+2}{Mn}Cl$

$+ 2H_2O$

ox aq $\{ \overset{+4}{Mn} \rightarrow \overset{+2}{Mn} \quad +2e$

red aq $\{ Cl^{-1} \rightarrow \overset{0}{Cl} \quad -1e$

properties of chlorine

1. extremely reactive - attacks metals
2. will replace both Br & I from KBr & KI

$KMnO_4 + NaCl + H_2SO_4 \rightarrow$

$2NaCl + H_2SO_4 \rightarrow HCl + Na_2S$

$2K\overset{+7}{Mn}O_4 + 10NaCl^{-1} + 8H_2SO_4 \rightarrow$

$5\overset{0}{Cl_2} + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H$

$+ 5Na_2SO_4$

aq $\{ \overset{+7}{Mn} \rightarrow \overset{+2}{Mn} \quad +5e$

aq $\{ Cl^{-1} \rightarrow \overset{0}{Cl} \quad 1e$

Prep

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + H$

Prop of HCl (gas)

colorless - gas
sol in H_2O

HCl (acid)

1. action on metals
$Zn + HCl \rightarrow ZnCl_2 + H_2$

2. action on metallic oxides

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$

3. action on metallic Hydroxides
(neutralization

$NaOH + HCl \rightarrow NaCl + H_2$

4. action on salts such as
carbonates

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2C$

$\downarrow$

$H_2O + C$

5 action of HCl with ox agents

$HCl^{-1} \longrightarrow \overset{0}{Cl_2}$

$KMnO_4 + NaCl + HCl \rightarrow MnCl_2 + Cl_2 + KCl + H$

oxygen [illegible]

oxides
- Cl_2O monoxide
- ClO_2 dioxide
- Cl_2O_7 heptoxide

oxyacids

chloric acid + chlorates

$HClO_3$ $KClO_3$

$KClO_4$ K perchlorate
monobasic acid

$$6KOH + 3\overset{0}{Cl_2} \rightarrow K\overset{+5}{Cl}O_3 + 3H_2O + 5K\overset{-1}{Cl}$$

ox ag $\overset{0}{Cl} - \overset{-1}{Cl}$

red ag $\overset{0}{Cl} - \overset{+5}{Cl}$

$$KClO_4 \xrightarrow{\Delta} 2KCl + O_2$$

Form#6
Local Mushroom

Dear Sir;

With all the stress now being placed upon the role of vitamins in national nutrition, don8t you feel that the mushroom has been left out of the picture?

We are prepared to conduct a very through survey of your process, which may reveal some very valuable information, as we specialize in the latest microbiological technic.

May we have a member of our staff call upon you to talk over this problem ?

Form#4
Special Professional

Dear Dr.....

We thought that you might like to know that we are now set up to run Thiamin assays according to the method of..... .

....

If you have an occasional sample which you would like to have checked with this method please feel free to call upon us. Of ~~course Doctor,~~ there will be no charge .

Very truly yours

Form #5

Professional

Dear Dr.....

You no doubt have felt the need for rapid methods of assay for members of the B complex, which would still retain the value of biological methods.

We feel that the microbiological methods of Snell, Strong, Fry ..... and other workers in this field answer this problem. We are now making assays using these methods, and checking biological results within the limit of error inherent in the rat and and chick assays.

The rapidity with which these assays may be made make them particularly valuable in checking the effect of various processes upon the vitamin content of foodstuff.

At any time you feel that you could use our services, please call upon us. we will be happy to cooperate with you.

Very truly yours

O.H.SEibert

p1 The stress now placed upon the role of vitamins in National Nutrition makes it very important for the candy manufacturer to consider this question.

p2 More and more manufacturers are turning to fortifying their products with vitamins. One serious obstacle to this fortification was the need for rapid assay methods. With biological methods weeks were needed for complete results, so that when the assay was finaly completed its value as a process control was lost.

p3 We are prepared to give rapid accurate assays using microbiological technic which has proven very succesful, particuliarly with dark colored samples which have proven difficult with optical methods.

p4 May we assist you with your vitamin problem ?

Drying Macine Co.s

6/6/40

I. The stress now placed upon the role of vitamins in National Nutrition makes it very important to consider this question when drying foodstuffs.

2. The prospective purchaser of your equiptment is almost certain to inquire as to the possible effects of your method of drying,upon the vitamin content of his product.

3 Can you answer this question quickly?

$4 We are prepared to give rapid accurate assays using microbiological technic which has proven very succesful particuliarly with dark colored or turbid samples which have proven difficult with optical methods.

5. May we assist you with your vitamin problems?

FORM I
Yeast Co.s

November 8, 1941

Red Star Yeast & Products Co.,
3915 Wissahickon Avenue,
Philadelphia, Pennsylvania.

Gentlemen:

I. The need for fast, accurate assay results has long been recognized as a serious bottle-neck in the industrial application of vitamin control, fortification or extraction.

"2. Users of yeast today are extremely anxious for immediate answers to questions about vitamin content of your products. Frequently, the ability to supply these answers means the difference between winning or losing a contract.

3, We are equipped to supply immediate analysis of all vitamins using the most modern methods which have been found to check very favorably with the time consuming biological assays.

4 May we assist you with your vitamin problems?

Very truly yours,

Form #4
General

Dear Sir;

I mustn't shout because Terry insists that it's bad form, but have you ever thougnt how extraorinarily difficult it is to compose a letter wnich conveys how good you are without being irritatingly blatant ?

We for instance, realy feel that we equipted to give very rapid results on the B complex using the microbiological technic which has reduced the time element to a matter of days as compared with the weeks necessary for the biological methods.

We do certainly take pride in the exceptionaly accurate assays we have made on dark colored samples which had proven amost impossible with fluorometric methods, but it would never do for us to splash letters about saying we were better than any one else.

After all we may only be imagining it,...But May we help you with your vitamin problem ?

Very Truly Yours

O.H. Seibert

December 1, 1942.

Mr. A. Brothman,
420 Lexington Avenue,
New York, N.Y.

Dear Sir: Re: Treatment and analysis of spent Ni catalyst

Following is an outline of results and calculations on the above problem:

Sample #1. Original

2 gms + 36 ml. of aqua regia digested for three hours on water bath and finally boiled for fifteen minutes over a direct flame.

16.1907 gms. cruc.	ppt.
15.9081 " "	#5
0.2826 gms. ppt.	

Calculation

$$\frac{0.2826 \times 0.2031 \times \frac{250}{25} \times 100}{2.0000} = 28.8\%$$

Sample #2.

4 gms. + 80 ml. of 13% H_2SO_4 (1.09 C.P. Tr. 12° Be')

Digested for 1 hour in water bath at 83-84°C with aeration.

16.4604 gms. cruc.	ppt.
16.1354 " "	#1
0.3240 gms. ppt.	

Calculation

$$\frac{0.3240 \times 0.2031 \times \frac{250}{15} \times 100}{4.0000} = 27.5\% \text{ Ni}$$

Sample #3.

4 gms. + 10 ml. of 10% NaOH, and then 90 ml. of 13% H_2SO_4
Digested for 1 hour in water bath at 83-84°C with aeration.

16.0052 gms. cruc.	ppt.
15.6804 gms. cruc. #2	
0.3243 gms. ppt.	

Sample #3. contd.

Calculation

$$\frac{0.3243 \times 0.2031 \times \frac{250}{15} \times 100}{4.0000} = 27.5\% \text{ Ni}$$

Sample #4.

4 gms. + 10 ml. 10% NaOH, and then 90 ml. of 13% H_2SO_4 + 0.04 gm. of Fe Cl_3

Digested for 1 hour in water bath at 83-84°C with aeration

15.7567 gms. cruc. ppt.
15.4253 " " #
0.3314 gms. ppt.

Calculation

$$\frac{0.3314 \times 0.2031 \times \frac{250}{15} \times 100}{4.0000} = 28.1\%$$

(a) The recovery in Samples 2 and 3 is 95.5% and in the case of Sample 4 it is 97.6%.

(b) Because of the limitation of time on the above work - there would seem to be many angles on "recovery efficiency" which may bear further investigation.

B-1 IS BEST KNOWN AMONG VITAMINS

Survey Shows only 25% Think their use is a Passing Fad

By GEORGE GALLUP
(Director, American Institute of Public Opinion)

Princeton, Dec. 8.—One of the ost important developments in the eld of nutrition and dietary educa-ion has been the attention paid to tamins and calories—particularly itamins, which have been given an normous amount of publicity in e last decade.

The American Institute of Pub-ic Opinion has undertaken a na-onwide survey to measure the ex-nt to which information about itamins has penetrated the public ind, and to determine how many eople regard vitamins as nothing ore than a passing fad.

The results indicate that the ma-ority have heard about various spe-ific vitamins, particularly vitamin -1 in recent months, and that a bstantial number can name foods ch in any given vitamin. House-es are, however, hard put to de-ne a vitamin or to explain the dif-rence between a vitamin and a alorie.

ampaign Gaining

Only a small minority of the popu-ion believe that vitamins are a assing fad—evidence that the edu-ational campaign of health au-orities concerning vitamins has ccessfully penetrated the thinking f the majority of Americans.

The survey asked a series of ques-ons as follows:

"Is there any one vitamin which ou have heard a lot about in re-nt months?"

Vitamin A	7%
Vitamin B-1 (B and B-2)	42
Vitamin C	2
Vitamin D.	7
Other vitamins	2
Have not heard about any one vitamin in recent months	46

[Some persons named more than ne vitamin; hence the above totals ore than 100%.]

Approximately two-thirds of ose who were familiar with the rious vitamins correctly named ne or more foods containing those tamins.

elief in Importance

To determine people's belief in e vitamin theory and its impor-ance, the survey next asked the estion:

"Are vitamins a passing fad?"

The results follow:

Yes	25%
No	68
Don't know	7

Finally, as a measure of future ducational progress in this field, the Institute asked of housewives only:

"Can you explain the difference between a vitamin and a calorie?"

16%	made it plain that they understood the difference
84%	could not indicate the difference

The results show clearly that vitamin B-1, or thiamin, is the one which the public has heard most about in recent months. Isolated in large yields by Dr. Robert R. Williams, chemical director of Bell Telephone Laboratories, B-1 prevents the disease beriberi, helps check loss of appetite, excessive fatigue, nervousness and constipation.

It is found chiefly in lean po whole grain cereals and bre beans, peas, lentils, kidneys, eg liver, bran, wheat germ and yeast.

HASH MARKS

Service stripes are known as ha marks in the Navy.

FOOD MEN UNITE IN VITAMIN DRIVE

Continued From Page One

other authorities. Enthusiasm and interest then reached a new high, but no effective machinery for practical action was set up and food manufacturers now realize that the job is up to them. And the government has told them so.

"I am perfectly frank in saying," one government official declared recently, "that if you food manufacturers were to unite for action with the retailers, your power for education would far surpass any power of any government agency to promote the good cause of nutrition. We can only preach; you can put theory into daily practice."

Attempts to do so have already been made, of course, and the bread industry has attempted to meet the need through featuring vitamin-enriched bread, manufacturers pointed out. The apathy with which its efforts were received by the public, however, indicated the need for an educational job. Individual food manufacturers, meanwhile, have been identifying their products with vitamins, but with such indifferent results that they have become convinced of the need of a coordinated effort.

Paul S. Willis, president of the A. G. M. A. group and spokesman for its food manufacturer members, concedes that the "job of nutrition promotion has to be done by the food manufacturer."

"A lot needs to be done in acquainting the public in what many of the discoveries in nutrition, such as vitamins, minerals and the others, mean to them in terms of health," he said recently. "We always had spinach, but it wasn't until 'Popeye' came along that people began to eat it in large quantities. We've got to tell the public what these things mean to them in terms they can understand."

That is what the food manufacturers have now decided to do.

Food Makers Unite to Promote Demand for Vitamin Products

Nutrition Program Aims to Regain Business Lost to the Drug Field—Educational Drive With U. S. Agencies Planned

By GEORGE A. MOONEY

Determined to wrest back from the drug trade the lucrative business in vitamins, food manufacturers were reported yesterday to have set in motion positive steps to increase consumer demand for nutritional foods through greater cooperation wit one another and with government agencies. While details of the plan have not been worked out, some of the broad principles have been established and a major point is the insistence that, while the program should be a long-term one, it must begin at once.

Representatives of food manufacturers have already begun a series of private conferences with government agencies, at which broad outlines of an educational plan have been discussed. It is fairly well established that neither the government nor the food men want to see a "high-pressure" campaign, but rather are aiming at coordination of advertising campaigns along lines primarily designed, first, "to educate the industry itself" and, second, to cut through the mass of confusing advertising statements that have been made about vitamins.

One possibility under discussion was that food men assist government agencies in preparation of a "master sheet" of simple definitions of the various vitamins, the qualities they possess and their uses. This would be used to guide the preparation of advertising copy to avoid public misconceptions, which are said to have been largely responsible for diversion of vitamin business to the drug trades from the food field.

A case in point was use of the term "nicotinic acid," which is commonly misunderstood because of its unpleasant connotation due to association of nicotine with tobacco. The vitamin, part of the B complex group, might be called the "anti-pellagra" food, and is found in milk, lean meat, eggs, green vegetables and some fruits.

That nutrition is of considerable public interest and a fallow field for the food industry is evident to most manufacturers, it was said. The Federal Government as long ago as March 5 called a National Nutrition Conference; the industry itself has undertaken sporadic campaigns to popularize nutritive values. Practical results in terms of real public understanding, however, have been small. Yet Governor Lehman's recent designation of the period Nov. 20 to 27 as Nutrition Week calls attention to the reality of that interest, it was pointed out.

Under the Selective Service examinations it was discovered that 50 per cent of the men called had to be rejected because of mental and physical defects, a large part of which were the result of malnutrition. The condition was dramatized by the President's calling of the special nutrition conference which was attended by leading educators, scientists, health and

Continued on Page Six

6/6/50
200

Doc:

Just get 3 and 4.

We already know of 1 and 2 and neither appear to be very [illegible] according to [illegible] them; [illegible] consuming [illegible] and [illegible] Photometer.

Hadoc

April 3, 1942.

Mr. Webb:

In addition to the enclosed rat assay method for vitamin B_6, you might suggest the following:

(1) J. V. Scudi; On The Colorimetric Determination Of Vitamin B_6. (J. Biol. Chem. 139: 707-720, June 1941)

(2) O. D. Bird, J. M. Vandenbelt, and A. D. Emmett; Adaptation Of The Scudi Colorimetric Method For Pyridoxine. (J. Biol. Chem. 142: 317-322, Jan. 1942)

These two are excellent chemical methods if one has a photoelectric photometer.

(3) The University of Texas Publication #4137, Oct. 1, 1941: Studies on the Vitamin Content of Tissue - I. Assay Method for Pyridoxine, p. 24 (A microbiological method). University of Texas is at Austin, Texas.

(4) M. Landy & D. M. Dicken: A Microbiological Assay Method for six B Vitamins Using Lactobacillus Casei and a Medium of Essentially Known Composition.

Sent to publishers Feb. 27, 1942 by Dr. Landy from Research Laboratories of S. M. A. Corp., Chagrin Falls, Ohio.

We have a pre-print, and the method developed seems to be excellent. This will appear shortly in The Journal of Clinical and Pathological Medicine.

K. Cartwright
Research Laboratory

KC:om

PYRIDOXINE ASSAY METHOD
(Anheuser-Busch Research Lab.)

The modified Halliday Evans method for the determination of pyridoxine (B_6) is carried out in our laboratories as follows:

Female weanling rats between 18-23 days old and weighing 40-45 grams are placed on a diet consisting of 73% beet sugar, 18% casein (Labco), 3% butter fat, 4% salt mix #1 (Merck), and 2% cod liver oil. They immediately receive the following daily supplements: thiamin hydrochloride - 25 micrograms; riboflavin - 20 micrograms; calcium pantothenate - 200 micrograms; nicotinic acid - 300 micrograms; choline chloride - 5 milligrams, and inositol - 5 milligrams.

On this regime typical acrodynia symptoms of pyridoxine deficiency develop within eight weeks. Our standard requires that at least four of the seven possible sites of severe lesions be involved before the animal can be considered ready for assay purposes. These sites are each forefoot, hindfoot, ear and the area about the nose. The animals should also show a plateauing in weight gain or a gradual loss in weight as the symptoms begin to appear.

When the animals are depleted they are divided into groups of eight for assay purposes. No two litter-mates are ever included in any one group. One group of four animals is maintained on the basal depletion ration as negative controls, a second group of eight is given 10 micrograms of crystalline pyridoxine hydrochloride daily as positive controls. The balance of the groups are used for assay purposes and are supplied with that amount of material being tested which is calculated to furnish a daily supplement of 10 micrograms of pyridoxine.

Since this is a curative method of assay each animal is scored as to the number and intensity of the lesions as well as to its weight. When groups are made up it is desirable to keep the number and intensity of the lesions as nearly constant as possible in all groups. The average weight should also be kept fairly constant.

The depleted animals are very susceptible to a number of recurrent infections and a weight record is kept to indicate freedom from such infections. When the animals are properly supplemented and free of infections they will respond with remission of symptoms and gain in weight over the four week assay period. Failure to gain weight indicates an infection but usually does not interfere with the remission of acrodynia symptoms, which is the real test of pyridoxine content.

Materials containing large amounts of unsaturated fatty acids cannot be successfully assayed by this method, for several fatty acids cause a remission of the symptoms for a period longer than that used for the biological assay.

The modifications included in this assay technique include:

(1) Substitution of beet sugar for cane sugar which was shown by Bender & Suplee, J. Nutrition 20, Feb. 1940, to contain appreciable amounts of pyridoxine. We confirmed this in our laboratories.

(2) We found it very difficult to free the so-called filtrate factor of pyridoxine and successfully substituted calcium pantothenate for filtrate factor.

(3) There is no preliminary depletion period and the animals receive all of the essential factors except B_6 from weaning on. We have included choline and inositol in addition to the four synthetic vitamins of the B-complex.

(4) Nicotinic acid promotes ear involvement.

The literature references concerning this method and the modifications, are as follows:

(1) Györgyy, P.:Biochem. J. 29, 741, (1935)

(2) Halliday, M. & Evans, E. F.: J. Nutrition 13,(June,1937).

(3) Edgar, C. L., El Sadr, M. M., Macrae, T. F.: Biochem. J. 32, 2225,(1938).

(4) Wooley, D. W., Waisman, H. A., Elvehjem, C. A.: J. Biol. Chem. 129, 673, (1939).

(5) Jones, T. H.: J. Am. Chem. Soc. 61, 975, (1939)

(6) Bendor, R. C. & Supplee, G. C.: J. Nutrition 20, Feb.(1940).

(7) Griffith, W. H. and Wade, N. J.: J. Biol. Chem. 131, 567,(1939).

A

VITAMIN

ASSAY

LABORATORY

6/9/38

GENERAL The money is to be utilized to build and maintain a laboratory which will perform vitamin assays and also do certain clinical work.

In order to give a clear and complete picture of how we are going to carry out our purpose, the matter will be under the following headings:

1. The Vitamin Field
2. The Need for Vitamin Assays
3. The Customers
4. The Set-up of the Laboratory
   a) Personnel
   b) Construction
   c) Inventory of Materials

THE VITAMIN FIELD A rough working definition of vitamins are that they are minute amounts of matter occurring in certain foods which enable the human system to utilize what it eats. They are definitely essential for the maintainance of life. Thus, it has been demonstrated that it is actually possible for a person to become seriously ill by staying on a certain (and apparently excellent) diet for a period of time.

But the real field of vitamin work--especially in the United States--is not in dealing with complete vitamin starvation, but with borderline cases and continued chronic malnutrition; the seriousness of this matter has been recognized by our Government

and definite machinery has been set up, and is now functioning to carry out this work. Acting under the President's National Research Council, a Committee on Nutrition has been formed and already the following has been accomplished:

a) The millers are producing a package flour fortified with vitamin B 1.

b) The bakers have put out a vitamin B 1 bread.

c) An office of Nutrition has been formed under Dr. M.L.Wilson, a former Assistant Secretary of Agriculture to <u>inform</u> and <u>advise</u> (and here there is a very definite hint of force if necessary) the farmers, distributors, packers, processors, and any other groups connected with the food industry, just what they should do in order to make available to the Public foods with the highest possible nutritional value. The program which is being carried out consists of:

1. An immediate fortification of certain foods with synthetic vitamins as an emergency measure to prevent any further malnutrition.
2. A long range plan to increase the natural vitamin content of all foods and to teach the Public to buy on the basis of nutritional value, and not pounds per dollar. This educational plan is even now being put into effect in Philadelphia by means of the program of free lunches for <u>all</u> children.

2. THE NEED FOR VITAMIN ASSAYS Vitamin Assays, or the determination of the actual amount of vitamin present in a material, are absolutely essential to the carrying out of any such vast undertaking as that outlined above. The vitamins themselves are very fragile. They are affected, and sometimes completely destroyed, by heat, light, air, periods of standing, and even physical handling (such as grinding and crushing). Further, even for the same farm products the vitamin content varies tremendously depending on the location of the farm, the period of the year in which it was grown, and the method of cultivation of the soil. Obviously, then, to be of real value, the assays must be rapid. The methods of assay as they exist today are:

a) Biological. These involve testing the effects of standard amounts of the vitamin on large groups of animals (rats, guinea pigs, chicks) as compared with the material being assayed; these methods take from three to six weeks and are the ultimate standard since they measure the actual growth produced by the vitamin in question. We intend to do these but, in general, they take too long and are too expensive for ordinary work.

b) Microbiological. These measure the effect of the vitamin on the growth of a bacterium (i.e., a very small animal). They take from 3 to 5 days and are the most accurate known. We have had a great deal of experience in, and we intend to concentrate on, these methods.

c) Photometric. These measure the color produced by a reaction

of the vitamin and, as such, are not suitable for any food products which are almost certain to be highly colored. We shall not use these methods.

One of the principal aims of the Government control of nutrition is to do away with the vast amount of vague claims, misinformation and general outright quackery which is obscuring the real value of vitamins to the Public. Toward this end, rapid, accurate vitamin assays on all foods which are known to contain, or claim to contain vitamins, are necessary. In the very near future, it will no longer be possible for a chain store to proclaim "our meat contains the B vitamins" but they must state which of the six known factors of the B complex and how much of each. And this condition will apply to all foods and will not be temporary, and will become even more wide-spread as time goes on.

The Government is not set up and does not intend to be set up to perform these assays; it will be up to those in the food industry to have it done---and we propose to be the first in the field.

3. THE CUSTOMERS All of those actively working in the food industry are potential customers in that they would be vitally concerned in knowing the vitamin contents of certain products at definite times; for, as was explained above, the assay values vary tremendously even for the same food. We do not imply that all of these people would rush to have assays performed, but certainly they would help exert a mass pressure in this direction which would leave it squarely up to those who are most vitally affected, i.e., in their pocketbooks, to have these assays done.

6/6/50 gcs

Those who would pay to have assays done may be classified as follows:

a) Canners. Not only is it necessary for these people to know that the vitamins are present in a full measure to start with, but that their processing does not destroy a considerable amount. And this processing is different for the various products ranging all the way from string beans and spinach to fruit and vegetable juices. Also, after the assays had been run for a time, the canner would accumulate sufficient information on his sources of supply to enable him to buy intelligently with regard to the highest nutritional value. And, of course, the assay values themselves can be used as a fine advertising and sales point for the product.

b) Bakeries. The milling of wheat to produce white flour removes practically all of vitamin B 1. (thiamin). To counteract this, the bakers are producing a white bread which has been fortified with synthetic thiamin. Constant tests will have to be made to determine whether the thiamin is uniformly distributed through the loaf and whether the baking has done any harm.

c) Dairies. As in the case of the canners, the results of assays made over a period of time would tell them which farms produce milk of the highest vitamin value. Also, in the addition of vitamin D (dispersed in cream) to milk, a careful survey would seek out any harmful technique.

d) Candy Manufacturers. Here is a wonderful opportunity, and one which they recognize, for the makers of sweets to open a new field for the sale of many varieties of mints and candies. Again, vitamin assays will have to be done so that the actual amounts present can be stated on the box cover.

e) Container Manufacturers. The comparative ability of different types of light excluding, air tight, inert atmosphere, and anti-oxidant containers on the stability of the vitamin content of foods packaged in them is going to be a matter that these people will want to be able to answer in a direct and positive manner---in other words, they will need assays to back up their statements.

f) Drying Machinery and Other Food Processing Equipment Manufacturers. The makers of such equipment are going to have to answer the question "Will your machine lower the vitamin content of my food and, if so, how much?". Often this may be all that will stand in the way of closing an order. Certainly, it would be worth-while to these manufacturers to have assays made and then be able to say, "We have had your product tested before and after it has passed through our dryer (cooker, kettle, etc.) with the following results."

g) Check Work. Many laboratories of vitamin products which have their own assay laboratories have checks run on their samples outside by an independent laboratory; first, to

6/6/30

make certain that their own results are correct, and secondly, so that their customers may be doubly assured of the reliability of the assays.

h) Chain Stores. Big food chains (such as Penn Fruit, the A & P, and also Department Stores) could gain invaluable information for their purchasing department by having assays run. Of course, such information could be very nicely put to use by their advertising department. All of the above by no means cover the entire field of possible customers for vitamin assays for many others no doubt exist such as Doctors, Hospitals, and private individuals who might occasionally need such work done.

There can be no doubt that the field is big and promising.

4. THE SET-UP OF THE LABORATORY

a) Personnel. Four people are involved...Morrell Dougherty, Harry Gold, Dr. Francis Edel and Otto H. Siebert. The first two named are those who desire the loan; they are now employed at the PENNSYLVANIA SUGAR COMPANY. Dougherty and Gold are chemists and Dr. Edel has her Doctorate in Bacteriology. All three have been working in the vitamin assay field for the past year and a half.

Otto Siebert is of the firm of TERRY and SIEBERT, analytical chemists, which has been established since 1879 and has an enviable reputation in the sugar industry for accurate work.

As soon as the laboratory is ready, Dr. Edel, now employed in

4/5/40

Newark, N.J., would come to Philadelphia and work on full-time basis, we would in the meantime keep our present jobs; our share of the vitamin work would be done at night and the week end. Lest this seem like too much of a strain, it should be kept in mind that we have been doing pretty much the same thing at PENN SUGAR for the past year and working all kinds of fantastic hours. As soon as our laboratory was capable of supporting one man, then he would leave the Sugar Company, and so on.

We have had letterheads printed and are going to go ahead with writing individual, hand-tailored letters to possible customers in the various fields. These are not going to be any mimeographed high-pressure claims, but careful statements of facts, and will be addressed to a particular man (such as the advertising manager or chief chemist) by his name and title. Once the laboratory has been started, then individual appointments with these men can be made, in which we could go into detail as to how we would tackle their problem. Because of the long hours, we have been putting in, one of the two of us can take time off during the day without any difficulty. This brings us to the need for having the laboratory erected quickly, for these men are big men in their field and would no doubt want to inspect the facilities to see how the work is done.

b) Construction. One of us (Mr. Dougherty) will move to a house of the corner type having a store on the ground floor; this store will be converted into our small, compact labor-

atory; this will not only give considerable saving in rental, but have the additional advantage of having someone on the premises at all times.

A diagram of just how we propose to build the laboratory is given on the following page. In it we have embodied our own experience plus that of many other capable men. A good deal of the special apparatus and equipment we shall build either partly or entirely ourselves, because not only is that put out by the laboratory supply houses too expensive, but we can make them more to our own specifications that way.

c) Inventory of Material:

1	- Autoclave (15 lbs. pressure)	$125.00
1	- Refrigerator (second-hand)	60.00
1	- Centrifuge (plus tubes and other accessories)	58.00
1	- Analytical Balance (sensitive to 0.1 mg.)	75.00
2	- Laboratory Benches (pressed steel cabinets with home-made masonite tops)	200.00
2	- Laboratory Sinks	60.00
1	- P H Apparatus (glass electrode)	82.00
1	- Incubator (3-compartment for 20°, 37°, and 55° home-made cabinets)	110.00

Diagram of Laboratory

6/6/50

c) Inventory of Material (cont'd)

1. - Thiamine Assay Apparatus (glassware, heating element, thermo-regulator and motor to be bought--rest to be built)	$120.00
1. - Desk (second-hand)	30.00

Glassware

200. - Culture Tubes (special) at 7¢ each	14.00
24. - 5 ml. pipets	20.00
24. - 10 ml. pipets	24.00
12. - 1 ml. pipets	15.00
8. - 25 ml. pipets	6.00
6. - 50 ml. pipets	4.00
3. - 100 ml. pipets	3.00
12. - Beakers of each size from 50 to 2000 CC	30.00
3. - 2000 ml. vol. Flasks	6.00
3. - 1000 ml. vol. Flasks	5.00
3. - 500 ml. vol. Flasks	4.00
8. - 250 ml. vol. Flasks	10.00
12. - 100 ml. vol. Flasks	12.00
6. - 50 ml. vol. Flasks	4.00
6. - Pipet Racks	4.00
Tubing, Rod, Sample Bottles	10.00

The total is $991.00 and if we add $300.00 for starting an animal assay laboratory, the grand total is about $1300.00. The prices quoted are a trifle on the high side but, in general

are pretty close to what we would have to pay.

Otto Siebert's role is that his firm would give us immediately the prestige and reputation so necessary in work of this nature, which would take us a long time to establish.

Dr. Edel has her financial share of this undertaking.

A loan of $1400.00 would cover our part of the total money required with the following conditions:

a) We have enough starting capital to make the necessary initial moves; such as moving, and starting to get the laboratory in condition to receive the necessary equipment.

b) We would not wish to receive this loan before March 15 but, naturally, we must know immediately if we will ha it at that time, as we would not care to make the init expenditures, unless we were certain of the loan.

The loan requested would give us ample funds to start laboratory, plus running for the first three months af actually starting assay work.

As an added security, we would expect the bank to hold title to all equipment.

Attached to the last page are some clippings showing the nature and extent of the field and its possibilities...among these is

one very recent ruling by the Government, as of November 18th, 1941, to become effective May 18th, 1942, which practically make vitamin assays mandatory, and we feel that the first ones in this field devoted to vitamin assaying will have tremendous success.

Vitamin Rulings Become Effective On May 18, 1942

Labels Must Indicate What Proportion Of Avera Adult Daily Requirement Is Present In Prod

WASHINGTON—Final regulations governing the labeling of f for special dietary purposes, a classification which has generally assumed to cover vitamin capsules, were promulgated Novemb by Acting Federal Security Administrator Watson B. Miller. will become effective six months from that date, May 18,

The regulations differ only in minor textual changes fr proposed rulings issued by the Food and Drug Administra industry criticism last June. They require that the labels of and mineral products must specify not only how much such nutrient is present, but in the case of vitamins A, B_1, C, D and G, calcium, phosphorus, iron or iodine, they must also indicate what proportion of the average adult daily requirement is present.

The following are the average daily requirements specified: Vitamin A, 1500 USP units for infants, 3000 units for children, 4000 units for adults; vitamin B_1, 0.25 mg. for infants, 0.5 mg. for children under six, 0.75 mg. for children six or over, 1 mg. for adults; vitamin C, 10 mg. for infants, 20 mg. for children, 30 mg. for adults; vitamin D, 400 USP units; vitamin G, 0.5 mg. for infants, 2 mg. for adults; calcium, 750 mg. for children and adults, 1.5 mg. for pregnant or lactating women; phosphorus, 750 mg. for children and adults, 1.5 mg. for pregnant or lactating women; oron, 7.5 mg. for children under six, 10 mg. for children six or over and adults, 15 mg. for pregnant or lactating women; iodine, 0.1 mg. for children or for adults.

These regulations on "special dietary foods" have been the source of much controversy, and several hearings have already been held. It is significant that the regulations never mention the words "vitamin capsules" or "vitamin tablets," and that many of the provisions are specifically concerned with the addition of vitamins and minerals to natural foodstuffs.

that vitamin capsules should be considered "foods" and not "drugs," and because FDA officials have several times indicated that in their opinion vitamins may be either foods or drugs depending upon the particular use to which they are put, it has been generally understood that the regulations will apply also to the vitamin concentrates.

According to the regulations, if the need for a given vitamin in human nutrition has not been established, the label must bear, in addition to a statement of the quantity of the vitamin, the phrase: "The need for — in human nutrition has not been established," the blank to be filled in with the name of the vitamin.

(Continued on Page 22, Column 5)

December 1, 1941

Final Regulations Given On Vitamins

(Continued from Page 3, Column 4)

Food products represented as a means of regulating the intake of protein, fat, carbohydrate or calories for the purpose of controlling body weight, or for dietary management, will be required to bear a statement on the label showing the per cent by weight of protein, fat and available carbohydrates and the number of calories supplied by a specified quantity of such food, according to a section of the regulations that have just been promulgated.

"45 MILLION AMERICANS ARE VICTIMS OF VITAMIN STARVATION"

—OFFICIAL U.S. GOV'T ESTIMATE, 1940—

DID YOU KNOW

that ⅓ of all Army Draftees rejected, had Vitamin deficiency ailments . . . Official U. S. Health Department figures are astonishing—Actually millions of Americans, rich and poor, are tired, listless, run-down . . . *losing their youth, buoyancy and vitality without even suspecting the cause!*

"C" THE NEGLECTED VITAMIN!

It's so easy to be lacking in Vitamin "C". Only a few foods contain enough of it. Cooking with soda or boiling destroys it. Alcohol, overwork, colds or common infections rob your system of it. You may be rich or poor, or eat like a horse, and still be deficient in Vitamin "C".

WHY YOU NEED "C" DAILY

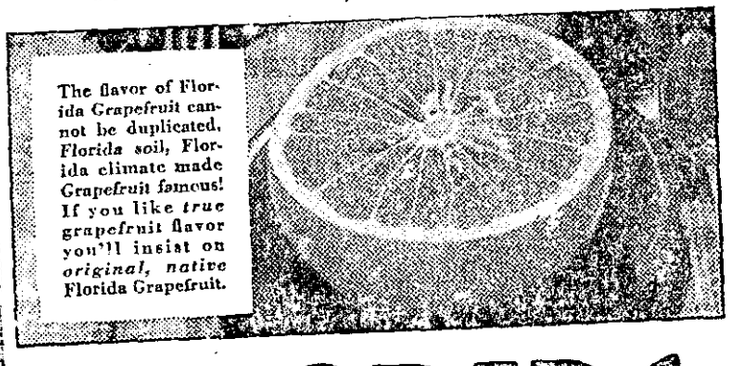
Your body does *NOT* store Vitamin "C". Unless you replace it daily—in sufficient quantities—your *system is going to feel it!*

WHEN NATURE WARNS YOU!

If you suffer from frequent colds, if your bones ache, if you bruise easily, if your gums are soft, if wounds and cuts don't heal quickly, if you feel "too old and tired"—*then watch out!* These are the "danger signals"—*go see your doctor!* You're probably very low in Vitamin "C".

FLORIDA GRAPEFRUIT IS "LOADED" WITH VITAMIN "C"

There's no need to buy Vitamin "C" in pill form, delicious Florida Grapefruit will furnish *ALL* the Vitamin "C" you need every day. You get it *FREE* in the cost of your food—and you get it in *natural* form . . . along with B_1 and B_2 and valuable minerals and fruit sugars for extra energy. Ask your dealer for *FLORIDA GRAPEFRUIT* today. It's really delicious!



FRESH **FLORIDA GRAPEFRUIT**

YOUR DAILY FRUIT

SAC 6/26/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

65-4307-1-B-5 (29-15)

Re memo 6/8/50 on GOLD residence search material.

On June 21, 1950, GOLD identified the material in the above folder as being concerned with mixing data, and thinks that this is part of the material BROTHMAN wrote on mixing. GOLD stated he did not know why he still had this in his possession, but stated that there were three possibilities as follows:

1. that BROTHMAN later submitted the complete report on mixing data in late 1942.
2. that this is material GOLD got from BROTHMAN subsequent to the time BROTHMAN gave him a complete report on mixing equipment, which would place the time of delivery, according to GOLD, on the instant material as in 1943.
3. a slight possibility that GOLD obtained it from BROTHMAN while he was working for BROTHMAN from 1946 to 1948.

GOLD stated that the nomographs which accompanied the typewritten pages were also concerned with mixing, and which GOLD believes were drawn by OSCAR J. VAGO.

GOLD stated that none of his handwriting or handprinting appears on any of the pages comprising the above exhibit, and feels that the handprinting shown therein is that of ABRAHAM BROTHMAN.

TSM:cab
65-4307

SAC

6/3/50

SA WILLIAM H. NAYLOR

HARRY GOLD, was.
ESPIONAGE - R

RE: GOLD RESIDENCE SEARCH MATERIAL

Exhibit No. 65-4307-1-B-5 (29-15)

Reference memorandum, 6/6/50, Page 15.

Description:

Twenty-four pages, including Page 18A, of typewritten material captioned, "An Approach to the Problem of Continuous Reactor and Combining Equipment Design". This material is accompanied by thirteen additional typewritten pages of illustrative examples.

Two sheets of tracing paper, one of which reflects Nomograph I, captioned "Theoretical Circulating Capacity of Turbine Type Agitators", while the other reflects Nomograph II, captioned "Theoretical Circulating Capacity of Propellors at 100% Slip".

Three sketch sheets from Chemurgy Design Corporation, reflecting the following drawings:

Figure I - "A High Efficiency Continuous Mixing Vessel"
Figure 2 - "A Continuous Combining System Comprising a Series of Vessels."
Figure 3 - "An Idealized Representation of Figure 1."
Figure 4 - "Continuous Mixer Without Draft-Tube"
Figure 5 - "A 'Compartmentalized' Continuous Combiner"

Possible Leads:

No apparent leads other than possible use of material in questioning GOLD regarding work in this field.

WHN:ams
65-4307

AN APPROACH TO THE PROBLEM OF CONTINUOUS REACTOR & COMBINING EQUIPMENT DESIGN

One of the prime objectives of production men and plant designers has always been to put all plant operations on a rationalized "assembly-line" basis------to put each unit operation in a manufacturing sequence on a basis such that the given operation provides a uniform, steady, and continuous feed for its sequel. Especially today, with the United States on a war footing and production one of the most vital elements in bringing this war to a quick and victorious end, rationalized production is high on the list of "musts". The advantages to the chemical and process industries of "assembly-line" production --- of the ability to continuously feed raw materials in one end of a plant, to flow continuously through all of the unit operations involved, and finally to discharge continuously for disposition at the other end of the plant---would include:-

1. the elimination of all "dead-time" in charging and discharging batch types of equipment, in bringing an accumulated mass of material to appropriate processing levels of temperature and pressure, etc.------, thereby increasing the productive time of a plant
2. a reduced requirement for highly trained personnel from the already-strained manpower reservoir
3. greater uniformity of products through the elimination of the human element in control
4. a pronounced decrease in the cost of production
5. in most cases, a greater productivity per volume of tankage per unit of time.

It is the purpose of this article to present a rational method for designing continuous equipment for handling those combining phenomena (reactions,

dissolving, b[redacted]ing, emulsifying, etc.) in [redacted] li uid phase enters as the principal means of the combining phenomenon and which are characterized at times by comparatively low ~~combination~~ combining velocities. This development, the authors believe, fills in one of the last remaining links in making "assembly-line" production possible for the process and chemical industries. The notable success which has typified the use of continuous calciners, kilns, attrition and grinding mills, vapor phase reactors, stills, filters, centrifuges, dryers, crystallizers, etc. as well as the continuous equipment for handling all other chemical engineering unit operations, it is our belief, will spur the utilization of the following material.

In Fig. 1, what the authors consider to be a continuous mixing vessel of high efficiency is illustrated. However, the construction shown should not be regarded as a specific recommendation in any respect, since a large number of other specific arrangements for the indicated "elements" can be gainfully employed to satisfy the general operational characteristics of the device shown. In fact, other specific arrangements embodying the principles of operation shown in Figure 1 may be more advantageously suited to certain particular instances.

Let us proceed to break down the structure shown in Fig. 1 into its elements, and investigate each of the elements with respect to the direct function/s each serves.

(A) The direct functions served by the draft tube are:-

(1) to "channelize" the path of travel of the incoming stream, so that the new feed is subjected

to the very intensive mixing action which exists in the immediate neighborhood of the "homogenizing" mixers.

(2) to restrict to some approximate predictable limit the smallest length of time which a particle could spend in the mixing unit by defining the average course via which the particle will travel from inlet to outlet nozzle.

(B) The direct function served by the recirculation ports in the draft tube is to permit a recycling of a portion of the material which was previously exhausted from the draft tube, back into the draft tube and down thru the "homogenizing" and exhausting mixer elements.

(C) The direct functions served by the "homogenizing" mixers are:-

(1) to provide an optimum condition of agitation under which the reacting or combining action proceeds.

(2) to provide for the fullest possible blending of the incoming stream with the previously fed materials that are being recirculated thru the ports in the draft-tube.

(D) The direct functions served by the draft-tube exhausting mixer are:-

(1) to cause a constant "turnover" of materials in the mixing vessel by continuously exhausting the contents of the draft tube.

(2) to [illegible] augment the "homogenizing" mixers' effects in certain sizes of mixing assemblies, the draft-tube exhausting mixer element may perform both the functions of providing the draft-tube exhausting action and the "homogenizing" mixers' effects. It may also be pointed out here that in most instances, propeller or turbine type mixers would be used to discharge the pumping function of the draft-tube exhausting mixer. Although paddles (of either the "pitched" or normal blade types) could, if assigned the proper speed, perform the required task, turbines and propellers, if properly designed, and assigned proper operational characteristics, would perform with greater efficiency than paddle type mixers.

(E) The direct functions served by the mixing vessel and the inlet and outlet nozzles are, of course, obvious.

A cursory examination of the mode of operation of the equipment shown in Fig. 1 reveals that, for the condition of continuous feed and continuous discharge, there does not exist any means whereby a uniform sojourn within the equipment for all portions of the feed is assured. In other words the effluent from the equipment would be made up of portions which had stayed for various periods of time in the system. Yet, it is known that the completion of combining phenomena does vary as some function of the time spent in the system. Since such is the case, the problem must be approached in the following manner if we are to be able to predict the

efficiency of a given continuous mixer.

The problem resolves itself into two main tasks:- firstly, it is necessary that we obtain some quantitative picture of the effluent from the equipment in terms of the times of stay in the system spent by each discreet portion of the effluent; and, secondly, the aforementioned quantitative picture of the effluent must be combined with the completion velocity characteristics of the combining phenomenon at hand in order to obtain the mean completion typifying the effluent. Expressed mathematically, it will be our goal to be able to compute the mean level of completion of a given combining phenomenon in the effluent from a continuous mixer after the manner set forth below:-

$$S = P_1 f(t_1) + P_2 f(t_2) + P_3 f(t_3) + \ldots\ldots\ldots P_n f(t_n) \quad (1)$$

WHERE:-

S = MEAN COMPLETION OF THE COMBINING PHENOMENON

$P_1, P_2, P_3, \ldots P_n$ = THE PROPORTIONS OF THE DISCHARGE RESPECTIVELY CORRESPONDING TO TIMES OF SOJOURN EQUAL TO $t_1, t_2, t_3, \ldots t_n$

$f(t_1), f(t_2), f(t_3), \ldots\ldots f(t_n)$ = THE EXTENTS OF COMPLETION OF THE COMBINING PHENOMENON AT HAND, IN TERMS OF FUNCTIONS OF $t_1, t_2, t_3, \ldots t_n$

To facilitate the discussion of the entire problem, we shall hereafter refer to the quantitative analysis of the effluent----the P_1, P_2, P_3, ...P_n of Equation (1)----as the "time-proportion" composition of the effluent.

Before we proceed with the detailed investigation of the problem, it would be well to note that various reasons might from time to time compel the use of a multiplicity of identical units in series. Such reasons might include the physical limitations as to vessel size imposed by a certain

factory building, the heat transfer surface requirements of the combining phenomenon at hand, etc. It is therefore apparent that the method which is arrived at for ascertaining the "time-proportion" composition of the effluent for units of the type shown in Fig. 1 must be sufficiently flexible to deal with cases where either a single unit or a multiplicity of vessels in series as shown in Fig. 2 will comprise the continuous combining system.

For any given rate of throughput and any stated number of vessels comprising the system, it will be seen from the development in this treatise that the "time-proportion" composition of the effluent can be obtained using the following easily-computed characteristic of the device shown in Fig. 1:-

a. the rate of turnover (or circulation) effected by the draft-tube exhausting device

The mean completion of any combining phenomenon, it will be shown, may be arrived at by using the "time-proportion" composition of the effluent (as determined in terms of (a), the rate of throughput desired, and the number and arrangement of vessels used) in combination with:-

b. the time vs. completion curve for the combining phenomenon in question

obtaining under:-

c. a given condition of work-input by the "homogenizing" and draft-tube exhausting mixers shown in Fig. 1

and

d. the volume of the mixing vessel shown in Fig. 1.

To develop the method of analysing the "time-proportion" composition of the effluent from one or a series of devices of the type shown in Fig. 1, Fig. 3 in which is illustrated an idealized diagrammatic representation of the fundamental actions and structures involved in the device shown in Fig. 1 will be used. Though Fig. 3 is employed mainly because it isolates the principal factors of the device shown in Fig. 1 for quantitative evaluation, it may well be pointed out that such a structure represents a workable continuous reactor or combiner that may be used in some instances in place of the unit shown in Fig. 1

Comparing Figs. 1 and 3, it can be seen that the pipe loop in Fig. 3 containing a volume of materials (V) is analogous to the mixing vessel, is circulated, or turned over, by a pump, which is analogous to the draft-tube exhausting mixer, at a rate of R units of volume per unit of time. The "feed" to the prescribed device is through the feed leg which is analogous to the inlet nozzle, and then passes thru that section of the piping which is marked ——————, and which serves functions analagous to those performed by the draft-tube contained in Fig. 1. The orifices, across which a prescribed loss in total "head" is taken, function analogously to the "homogenizing" mixers.

Using Fig. 3, we may now proceed to the task of evaluating the "time-composition" of the discharge for two cases of a single continuous mixer and for a series of identical continuous mixers. The approach is through the Algebra of Combinations.

Firstly, let us consider the case when a single continuous mixer is employed. If R gals. per min. is the rate of feed to the system, and if, as in all

cases of practical design R is substantially lower than the circulating capacity of the draft-tube exhausting mixer (gals. per min.) than the proportion of material which would leave the system after 1-pass from the inlet to outlet nozzles would be $\frac{R}{C}$.

(2) Let $p = \frac{R}{C}$.

It follows then that the proportion of material remaining in the system after one pass would equal (1-p); and hence the proportion of material leaving on the second pass would equal p (1-p). Similarly, if we were to continue the mechanics indicated above to obtain the values of the proportions leaving at the end of 3 passes, 4 passes, 5 passes, ———n passes; we would obtain the values set forth in TABLE1, below.

TABLE 1 B "TIME-PROPORTION" SERIES FOR THE EFFLUENT FROM A CONTINUOUS SYSTEM CONSISTING OF A SINGLE UNIT

B

TIME OF SOJOURN IN TERMS OF NO. OF PASSES COMPLETED.	1	2	3	4	5	6	7	8	n
PROPORTION LEAVING	p	pq	pq^2	pq^3	pq^4	pq^5	pq^6	pq^7	pq^{n-1}

Place on top ↓

TABLE 1A

PASS NO. LEAVING SYSTEM	PROPORTION LEAVING	PROPORTION REMAINING IN THE SYSTEM
1	p	$1-p$
2	$p(1-p)$	$1-p(1-p)-p = 1-p-p^2-p = (1-p)^2$
3	$p(1-p)^2$	$1-p(1-p)^2-p(1-p)-p = 1-p+p^2-p^3+p^2-p+p^2-p = (1-$
4	$p(1-p)^3$	
n	$p(1-p)^{n-1}$	

THAT IS if, q, is set equal to (1-p) it will be observed that the series generated takes the form of: p, pq, pq^2, pq^3, pq^4, etc., and is an infinite series whose summation value for all values of, n, going from 1 to ∞ is 1.

It is obvious from physical considerations that

(3) $$\sum_{n=1}^{\infty} pq^{n-1} = 1$$

since the sum of all the proportions must equal one.

If two identical vessels are operated in series, the shortest period of stay in the system must be 2 passes, 1 pass in the first vessel and 1 pass in the second, and the proportion of material leaving the system after such a stay is p^2. In other words, of the proportion (p) of 1-pass material leaving the first vessel a proportion equal to

(4) $$(p)(p) = p^2$$

would be discharged from the second vessel. There are two ways in which material may contrive to leave the two-vessel system after 3 passes:- (1) by making 1 pass in the first vessel and 2 passes in the second; and (2) by making 2 passes in the first vessel and 1 pass in the second. If we formulate these combinations, it will be noted that

(5) $$p(pq) + pq(p) = 2p^2q$$

would be the total proportion of material leaving the system after a stay of 3 passes. In words, of the proportion p which is discharged from the first vessel after a stay of 1-pass a proportion equal to pq would stay for 2 passes in the second vessel; while, of the proportion pq which is discharged after 2 passes in the first vessel a proportion p leaves the second vessel after a stay of 1 pass. The sum of the stated products would equal the total material staying in the system for a stay of 3 passes.

There are three ways in which material could stay in the system for a period of four passes:- (1) by making 1 pass in the first vessel and three in the second; (2) by making 2 passes in the first vessel and 2 passes in the second; and (3) by making 3 passes in the first vessel and 1 in the second. If we formulate these combinations, it will be found that:-

(6) $$p(pq^2) + pq(pq) + pq^2(p) = 3p^2q^2$$

would be the total proportion of material leaving the system after a stay of 4 passes.

In like manner, it will be found that there are:- 4 ways in which material may remain in the system for a period of 5 passes; 5 ways for a period of 6 passes; 6 ways for a period of 7 passes, etc. If we extend the mechanics of the operations illustrated above in Equations (5) and (6) to all subsequent sojourns in the system, we would obtain an infinite series in which the values indicated in TABLE 2 form the initial terms.

TABLE 2 "TIME-PROPORTION" SERIES FOR THE EFFLUENT FROM A CONTINUOUS SYSTEM CONSISTING OF TWO UNITS IN SERIES

TIME OF SOJOURN IN TERMS OF NO. OF PASSES COMPLETED	2	3	4	5	6	7	8	9	n
PROPORTION LEAVING	p^2	$2p^2q$	$3p^2q^2$	$4p^2q^3$	$5p^2q^4$	$6p^2q^5$	$7p^2q^6$	$8p^2q^7$	Cp^2q^{n-2}

If three identical vessels are operated in series, the shortest period of stay in the system must be three passes, and the proportion of material leaving the system after such a stay would be p^3. Stating the method whereby the proportion p^3 is obtained, it is readily noted that of the proportion p^2 which is discharged from the first two vessels after a stay of 2-passes

(7) $$p(p^2) = p^3$$

is discharged from the third after a stay of 1-pass in the same. If we were to set forth the number of combinations whereby a stay of 4-passes in a 3-vessel system could be arranged they would appear as follows against the proportions "travelling the indicated possible circuits": (SEE TABLE 3)

TABLE 3

Vessel #1	Vessel #2	Vessel #3	Proportions
2 passes	1 pass	1 pass	$(pq)(p)(p) = p^3q$
1 pass	2 passes	1 pass	$(p)(pq)(p) = p^3q$
1 pass	1 pass	2 passes	$(p)(p)(pq) = p^3q$
			TOTAL $= 3p^3q$

If the proportion of material leaving at the end of 5-passes in a 2-vessel system were to be similarly investigated, there would result (see TABLE 4)

TABLE 4

Vessel #1	Vessel #2	Vessel #3	Proportion
2 passes	2 passes	1 pass	$(pq)(pq)(p) = p^3q^2$
1 pass.	2 passes	2 passes	$(p)(pq)(pq) = p^3q^2$
2 passes	1 pass	2 passes	$(pq)(p)(pq) = p^3q^2$
3 passes	1 pass	1 pass	$(pq^2)(p)(p) = p^3q^2$
1 pass	1 pass	3 passes	$(p)(p)(pq^2) = p^3q^2$
1 pass	3 passes	1 pass	$(p)(pq^2)(p) = p^3q^2$

TOTAL $= 6p^3q^2$

Applying the above method of analysis for all succeeding sojourns in a 3-vessel system, we obtain an infinite series in which the values indicated in TABLE 5 form the initial terms:-

TABLE 5

"TIME-PROPORTION" SERIES FOR THE EFFLUENT FROM A CONTINUOUS SYSTEM CONSISTING OF THREE UNITS.

TIME OF SOJOURN IN TERMS OF NO. OF PASSES COMPLETED	3	4	5	6	7	8	9	n
PROPORTION LEAVING	p^3	$3p^3q$	$6p^3q^2$	$10p^3q^3$	$15p^3q^4$	$21p^3q^5$	$28p^3q^6$	$\frac{1}{2}p^3q^{n-3}$

The development of the "time-proportion" series illustrated above for the specific cases of 1,2, & 3-unit continuous systems is indicative of the fact that the proportion leaving a system of m vessels in series after a sojourn of n passes in the system is a function of m and n, and may be written:-

$$\phi(m,n) \qquad (8)$$

By the use of operations common to the Calculus of Finite Differences (notably by employing the concepts of Difference Equations and the LaPlace Generating Function), Brothman derived the general expression:-

(9) $$\phi(m,n) = \frac{(n-1)!}{(m-1)!(n-m)!} p^m q^{n-m} = \binom{n-1}{m-1} p^m q^{n-m}$$

for all values of m from 1 to ∞ and for all values of n from m to ∞

Since the sum of the proportions of comprising the discharge must equal 1, we can write:-

(10) $$\sum_{n=m}^{n=\infty} \binom{n-1}{m-1} p^m q^{n-m} = 1$$

The existence of Equation (10) fulfills the first step in our development,- namely the task of obtaining a means of computing the "time-proportion" composition of the effluent for a system consisting of one or more units of the type shown in Fig. 1. The time of sojourn, it will be noted, has thus far been evaluated in terms of the number of passes or cycles executed from the point of inlet to the point of discharge in one vessel. We may now evaluate the various sojourns in terms of normal time measurements by pointing out that in Fig. 3 the time (t_m) required for a single pass from inlet to outlet will be:-

(11) $$t_m = \frac{V}{Q}$$

since a condition of the design in both Figs. 1 & 3 is that the nozzles be so positioned as to make the statement as closely true as possible. All other steps or sojourns in the system would then take the form of nt_m, where n is the number of passes achieved.

We may now proceed to the task of incorporating the "completion vs. time" characteristics of the various combining phenomena into our development:- Consider firstly a First Order Reaction. The integrated form of a First Order Reaction Velocity Equation is:-

(12) $$t = \frac{2.303}{k_1} \log_{10} \frac{a}{a-x}$$

where:-

k_1 = the reaction velocity constant under a given condition of temperature, pressure, and agitation

a = the concentration of the starting reactant in mols per unit of volume in the reaction system

x = the depletion in concentration of the starting reactant in mols per unit of volume after a time interval of t

t = time of elapse after the reaction conditions of temperature, pressure, and agitation have been established.

We may write t in terms of nt_m (See Equation (11), and hence:-

(12) $$nt_m = \frac{2.303}{k_1} \log_{10} \frac{a}{a-x}$$

It is obvious that the completion of the reaction could be measured in terms of $\left(\frac{a}{a-x}\right)$, and hence we may write

(13) $$\lambda_1 n = \log_e \frac{a}{a-x}$$

where:-

(14) $$\lambda_1 = k_1 t_m$$

and, finally,

(15) $$\frac{a}{a-x} = e^{\lambda_1 n}$$

Similarly, $\left[\frac{b(a-x)}{a(b-x)}\right]$ as the measure of completion of a Second Order Reaction* may be written:-

(16) $$\frac{b(a-x)}{a(b-x)} = e^{\lambda_2 n}$$

where:-

(17) $$\lambda_2 = t_m k_2 (a-b)$$

And $\left[\left(\frac{a}{a-x}\right)^{\frac{1}{(a-b)(c-a)}} \left(\frac{b}{b-x}\right)^{\frac{1}{(a-b)(b-c)}} \left(\frac{c}{c-x}\right)^{\frac{1}{(b-c)(c-a)}}\right]$ as a measure of completion of a Third Order Reaction** may be written:-

(18) $$\left[\left(\frac{a}{a-x}\right)^{\frac{1}{(a-b)(c-a)}} \left(\frac{b}{b-x}\right)^{\frac{1}{(a-b)(b-c)}} \left(\frac{c}{c-x}\right)^{\frac{1}{(b-c)(c-a)}}\right] = e^{\lambda_3 n}$$

* This is the measure of completion for a bimolecular reaction when the two reactants are not present in stoichiometric balance.

** This is the measure of completion for a trimolecular reaction when no two of the three reactants are in stoichiometric balance with one another

where:-

(19) $$\lambda_3 = t_m k_3$$

$\left[\frac{C_s}{C_s - C_t}\right]$ as a measure of completion of a solids-dissolving or gas-dissolving operation may be written

(20) $$\frac{C_s}{C_s - C_t} = e^{\lambda_4 n}$$

where:-

(21) $$\lambda_4 = t_m A k_4$$

In The Above:-

t = Time of stay in system under desired conditions of agitation, pressure, temperature

k_2, k_3 = Reaction Velocity constants respectively for 2nd, & third order reactions under given conditions of temperature, pressure, and agitation.

k_4 = Solution velocity constant under given conditions of temperature, pressure, and agitation

a = Concentration of material (a) at start of reaction in Mols/V

b = Concentration of material (b) at start of reaction in Mols/V

c = Concentration of material (c) at start of reaction in Mols/V

x = Depletion in Concentration of any reactant in time t in mols per unit of volume

A = Area of contact between gas and liquid or solid and liquid phases in physical dissolving systems under given conditions of temperature, pressure, and agitation

C_s = Concentration at saturation limit of the solute in the solvent in Mols per unit volume

C_t = Concentration of solute dissolved under given conditions of temperature, pressure, and agitation at end of time interval t

From the above, it will be observed that when combining phenomena of the types treated with above are handled continuously $[f(t)]$ of Equation (1) will take the generalized form of:-

(22) $$[f(t)] = e^{\lambda n}$$

Thus for a system of m vessels (where m may equal a single unit or any number of vessels in series), Equation (1) may now be written, in view of Equation (22)

(23) $$S = \binom{n-1}{m-1} p^m q^{n-m} (e)^{\lambda n} + \binom{n}{m-1} p^m q^{n+1-m} (e)^{\lambda n+1} + \binom{n+1}{m-1} p^m q^{n+2-m} (e)^{\lambda n+2} \ldots$$

where S is the mean completion of the combining phenomenon in question as expressed in terms of the appropriate measures indicated in Equations (15), (16), (18), and (20), and λ is given its appropriate values according to (14), (17), (19), and (21). In view of Equation (19), we may write Equation (23):-

(24) $$S = \sum_{n=m}^{n=\infty} \binom{n-1}{m-1} p^m q^{n-m} e^{\lambda n}$$

By an extension of the mathematics leading to Equation (9) with special application to Equation (24), Brotheon derived the following explicit expression for (S):-

(25) $$S = \left(\frac{pe^{\lambda}}{1 - qe^{\lambda}} \right)^m$$

where the value of p, [illegible] are determined in accordance with our previous remarks. A qualification must be placed on the use of Equation (25). If we examine Equation (24) which contributes to the development of (25), it will be noted that S must have a finite value. This limitation arises from the fact that the laws of chemical equilibria restrict the completion of combining phenomena to

a finite level--in other words, no matter how complete a combining phenomenon may seem to be there exists some, at least infinitesimal, residue of uncombined material. If we test Equation (24) for the conditions under which (24) will be convergent by means of the ratio method for convergency, it will be found that where:-

(26) $$u_n = \binom{n-1}{m-1} p^m q^{n-m} e^{\lambda m}$$

where u_n = nth term of the given series

u_{n+1} must equal

(27) $$\binom{n}{m-1} p^m q^{n-m+1} (e^{\lambda})^{m+1}$$

u_{n+1} = (n+1)th term of the given series

and

(28) $$\lim_{n \to \infty} \frac{u_{n+1}}{u_n} = q e^{\lambda}$$

Where qe^{λ} is less than 1, Equation (24) will yield a finite value for (S). Equation (25) itself shows that (qe^{λ}) can never equal 1 and yield a finite value for (S). Hence the limitation on (25) is that (qe^{λ}) must be less than 1.

No treatment of the subject with a claim to utility could end with Equation (25) and the above-described limitation thereon. Indeed, it would be necessary to at least touch on the following questions pertaining to Equation (25):-

1) how can the effect of "homogenizing" mixing be considered?
2) how would reactions and physical combining phenomena involving heterogeneous systems be handled?
3) how would reactions whose completion vs. time curves deviate from their theoretical order be handled?
4) how would series reactions be handled?
5) how can the value of C, which enters in forming the value of p, be computed?
6) within what limits does t_m usually run?

The effect of "homogenizing" mixing in determining the efficiency of continuous combining expresses itself by its influence in determining the velocity characteristic/s of a particular combining phenomenon. In fact, three conditions may determine the velocity characteristic/s of a combining phenomenon. These are:- temperature, pressure, and, agitation. If the conditions of temperature and pressure are kept constant, the effect of agitation will be found to vary inversely with the extent of diffusivity of the combining materials with one another and/or with the dispersion medium. For any given condition of vessel design, any given tank design, and a given intensity of work-input, any one of three main types agitation conditions may exist. The three possible categories into which the agitation condition may fall include:-

a. a condition of non-uniformly-diffused turbulence
b. a condition of uniformly-diffused minimum turbulence
c. a condition of uniformly-diffused above-minimum (as referred to (b)) turbulence

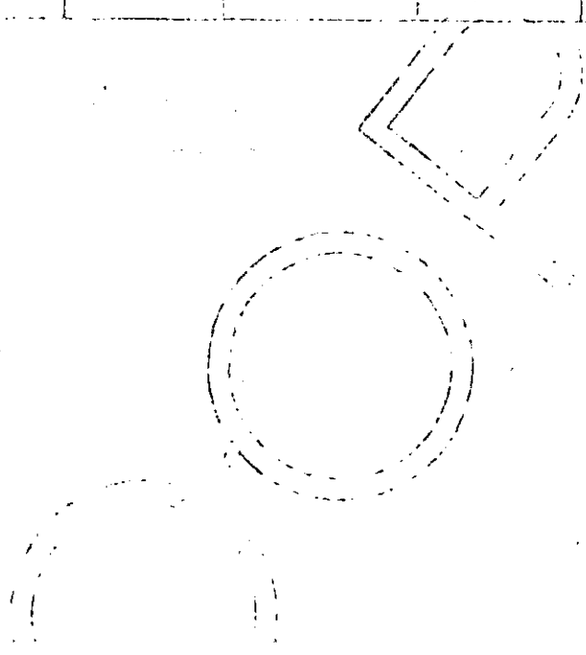
Condition (b) may be compared to that minimum level of linear velocity which, according to the concept of Reynold's Number, is adequate to establish, for a given viscosity, density and duct diameter a condition of turbulent flow. Conditions (a) & (c) are respectively below and above this point of transition to turbulence. The relation between reaction velocity constant and condition of turbulence in a combining unit is analogous to the relation between film coefficient and linear velocity in heat exchange equipment. For heat exchange equipment a critical level of turbulence exists beyond which an increase in turbulence will be accompanied by only a small increase in film coefficient. Likewise, for a mixing system a critical level of turbulence exists beyond which an increase in turbulence will be accompanied by only a small increase in reaction velocity constant. Thus, the most economical balance that can be achieved between film coefficient and work input to overcome friction drop in a heat exchanger is analogous to the most economical balance that can be achieved between reaction velocity constant and work input in the form of agitation in a combining system. Likewise, under normal circumstances the fluid velocity for optimum operating conditions in a heat exchanger is analogous to the level of turbulence demanded for optimum operating conditions in a combining system.

Table #6 is offered as a means of estimating three intensities of work-input which will establish, for containers of indicated volumes, conditions of agitation corresponding to Conditions (b) and (c) above.

The method of handling heterogenous reaction and physical combining systems may most often be considered to be a special case of handling the problems of continuous processing presented by reactions which deviate from known reaction orders (as will be treated below). This is true because the completion velocities

TABLE 6: APPROXIMATE MIXER HORSEPOWER REQUIREMENT

TANK CHARGE (Gallons)	Medium Agitation			Rapid Agitation		
	Thin	Medium	Viscous	Thin	Medium	Viscous
1 - 2	1/100	1/100	1/30	1/100	1/30	1/20
2 - 5	1/100	1/30	1/8	1/30	1/20	1/8
5 - 10	1/30	1/30	1/8	1/20	1/8	1/4
10 - 25	1/30	1/8	1/4	1/3	1/4	1/3
25 - 50	1/8	1/4	1/3	1/4	1/3	1/2
50 - 100	1/4	1/3	1/2	1/3	1/2	3/4
100 - 200	1/3	1/2	3/4	1/2	3/4	1
200 - 400	1/2	3/4	1	3/4	1	1½
400 - 600	3/4	1	1½	1	1½	2
600 - 1000	1	1½	2	1½	2	3
1000 - 1500	1½	2	3	2	3	5
1500 - 2000	2	3	5	3	5	7½
2000 - 3000	3	5	7½	5	7½	10
3000 - 5000	5	7½	10	7½	10	15



of heterogeneous systems involve consideration of the area of contact between the combining phases, and because the said area factor is not usually susceptible of quantitative evaluation. Hence, as for the case of combining phenomena which deviate from the known reaction orders, empirical relationships between completion levels and time are therefore the usual form which such data takes.

The job of handling reactions which deviate from their theoretical reaction orders falls into two separate categories:-

a) the job of handling reactions which despite their apparent theoretical classification obey the laws of another order (as for the case of theoretical second order reactions which obey the law of a First Order Reaction, and which are hence pseudo-unimolecular reactions);

and,

b) the job of handling reactions which do not conform to any known reaction orders

The handling of Category (a) reduces to gauging the completion of such phenomena by the methods applying to the reaction order which they do follow in fact. The task of computing systems which belong to Category (b) reduces to two operations:-

a. obtaining an empirical equation for the completion vs. time curve demonstrated by the combining system under certain processing conditions of temperature, pressure, and agitation, and formulation. Such equations should be set in the form

(29) $$t = \varphi(C)$$

when C is the completion characteristic for the given system

and,

b. using the ~~curve~~ empirical equation in the manner which will be demonstrated below for the case of a bimolecular reaction in which the starting reactants are present in stoichiometric balance.

The integrated form of the reaction velocity equation for the cases where two identical molecules, or two different molecules in strichiometric balance with one another, are reacted is:-

(30) $$k_2 t = \frac{x}{a(a-x)}$$

where:-

k_2 = reaction velocity constant under a given condition of agitation, temperature, and pressure

a = starting concentration of both reactants in moles per unit of volume

x = the depletion in concentration of both reactants at the end of a time interval t

As above, t may be written equal to (nt_m) and hence:-

(31) $$k_2 n t_m = \frac{x}{a(a-x)}$$

Therefore where $(e)^{\frac{x}{a(a-x)}}$ is used as a measure of completion of such a reaction, it will be found that:-

(32) $$(e)^{\frac{x}{a(a-x)}} = e^{\lambda n} \quad \text{where:-} \quad \lambda = k_2 t_m$$

Hence, where the mean value of $e^{\frac{x}{a(a-x)}}$ in the effluent from a continuous set-up is desired

(33) $$\left[e^{\frac{x}{a(a-x)}}\right]_{mean} = S = \left[\frac{p e^{\lambda}}{1 - q e^{\lambda}}\right]^{m}$$

The problem of series reactions ~~physical~~ or combining phenomena may be taken to include:-

a) those combining phenomena which demonstrate different completion velocity constants at various periods during the processing operation

b) those combining phenomena in which ~~simultaneous~~ simultaneous phenomena occur during the processing operation, or in which the product of one reaction is a reactant in a simultaneous reaction.

Those phenomena which fall into ( ) must be considered by dealing with each time phase - each phase of the operation to which a distinct andconsistant value for the completion velocity constant may be attached - as a separate problem involving a continuous set-up for that particular time phase. Thus, the total system would be a summation of equipment to accomplish each time phase. Combining phenomena involving several simultaneous individual phenomena must be considered as ~~with the case where~~ reactions following no known order, since in such cases only empirical completion vs. time curves and equations can be drawn.

The values of Θ for turbines and for propellers may be obtained by the use of Nomographs I and II respectively. For general design purposes, it should be noted that the values of t_m for most usually-encountered sizes of equipment run from slightly above 1 sec. in one-gallon holding capacity vessels to 1.5 mins. in 2500 gals. holding capacity units.

In general, it should be observed that the mathematical conclusions set forth above are not restricted in their applicability to the device shown in Fig. 1. Let us consider, for instance, a vessel of the design shown in Fig 4 in which a single mixer engages a liquid mass uniformly. It is notable that the design in Fig. 4 differs from that in Figs. 1 & 3 only in that a draft-tube is not employed. If a system comprising units of the type shown in Fig. 4 were computed on the basis that a draft-tube were present theoretically, what might we expect of the thus-computed results? It follows ~~therefore~~ that since the role of draft-tube in restricting the possible times of sojourn in the system to integral multiples of the theoretical turnover-time is eliminated in Fig. 4, some deviation ~~from actual results~~ would ~~result from the application~~ exist between actual and computed results.

~~to Fig. 4 of the above mathematical theory.~~ It will be found however, that the more uniformly the mixer engages the liquid mass in instances where draft-tubes are not used the smaller is the deviation of the computed results ~~applying the above methods of computation~~ from the actually-achieved results.

Again, let us consider a "compartmentalized" continuous combiner of the design shown in Fig. 5 Here, it will be seen that two design limitations contained in Figs. 1 & 2 are not present. Firstly, the mixing units do not work in conjunction with either a common draft-tube or individual draft-tubes. Insofar as the use of individual draft-tubes are concerned, the remarks made above are pertinent. Insofar as each unit is "compartmentalized" away from the other mixers and insofar as the mixers do not function in connection with a common draft-tube, each of the compartments may properly be considered to constitute an individual continuous unit and the composite unit a series of three continuous combiners. The second difference between Fig. 1 & each compartment of Fig. 5 is that the point of exit for each compartment is not located in the immediate vicinity of the point of feed. In fact, the minimum possible time of sojourn in terms of $\frac{V}{Q}$ where $\frac{V}{Q}$ equals t_m would equal approximately $\frac{1}{2}\ t_m$ since the point of exit for the effluent from each chamber is ~~diametrically~~ directly opposite the point of entry. It is apparent then that Equation (24) would then take on the form

$$(34) \qquad S = \sum_{n=m}^{n=\infty} \binom{n-1}{m-1} p^m q_0^{n-m} e^{\lambda(n-\frac{1}{2})}$$

It may then be shown that the completion achieved in the effluent for a particular operation carried on in a unit as shown in Fig. 5 would modify (25) to:-

$$(35) \qquad S = e^{(m-\frac{1}{2})\lambda} \left(\frac{p}{1-q_0 e^{\lambda}}\right)^m$$

where in the indicated case m has a value of 3.

In summary on this point, we are privileged to conclude that the general approach set forth above will apply to all cases of continuous combiner design which follow in even the most general way the basic mode of operation described for Fig. 1. Specifically, any continuous mixer design employing an agitator unit which tends to approach a full and theoretically uniform turning-over of a tank-mass may be computed on the basis of the theory given here, subject to the qualifications set forth above. It should be noted that ~~the~~ all other than (34) & (35) formulae, as set forth above and used hereafter apply specifically to cases where a full analogy to the idealized diagram, Fig. 3, obtains.

The following problems will illustrate the use of the above material:-

Illustrative Example I

An existing plant contains ten identical reactor vessels operating "batchwise" to carry out the following reaction:

$$A + B \rightarrow C + D$$

The reaction follows, as would be expected the normal curve for a Second Order Reaction. The initial concentrations of A and B are 10 mols per liter and 5 mols per liter, respectively. The number of mols of A and B reacting in 3 hours is 4. Or, at the end of 3 hours the mol percent completion of reaction referred to reactant B is 80%. The time consumed in charging the vessels is 20 minutes. The discharging time is ten minutes. The time required to bring the batch in each vessel up to reaction temperature, by means of internal steam coils is 45 minutes; and, no appreciable amount of reaction takes place prior to the time when the vessel's charge is brought to the final processing temperature.

Each vessel has a diameter of 4'-0" and a straight side vessel height of 6'-0". The holding capacity of each vessel is 610 gallons. However, the vessels are "worked" batchwise at 75% of their total holding capacity. Each vessel is equipped with a top-entering dual-propeller mixing assembly consisting of two 8" diameter x 14.5" mean pitch three-bladed marine propellers rotating at 1125 R.P.M. The propellers are located $\frac{1}{4}$ and $\frac{1}{2}$ the way up from the vessel bottom, respectively.

(a) What is the batch-operation capacity of the plant?

(b) What is the increased continuous-operation capacity of the plant assuming the same percentage of completion

for the reaction is desired, i.e.

(1) the two vessels are placed in series?

(2) two parallel systems of five vessels in series are used?

(3) five parallel systems of two vessels in series are used?

(4) ten parallel systems of one vessel in series is used?

(c) Assume that instead of an increased plant capacity for turning out 80% completely reacted material, a higher percentage of completion is desired for the plant's present productive capacity. It is hoped that thereby costs of "working" a distillation for the recovery of unreacted A & B may be reduced or eliminated. To what extent can this be accomplished if condition (1), (2), (3), or (4) under (b) is used?

-#-#-#-#-#-#-#-#-#-

(a) The batch-operation capacity of the plant in g.p.m. can be found from the following considerations.

The total processing time per batch is the sum of the charging time, heating-up time, actual reaction time, and discharging time, or:

= 20 mins. + 45 mins. + 3 hrs. + 10 mins.

= 4.25 hrs.

Where 610 gals. is the total holding capacity of each vessel, the batch sizes run will be:

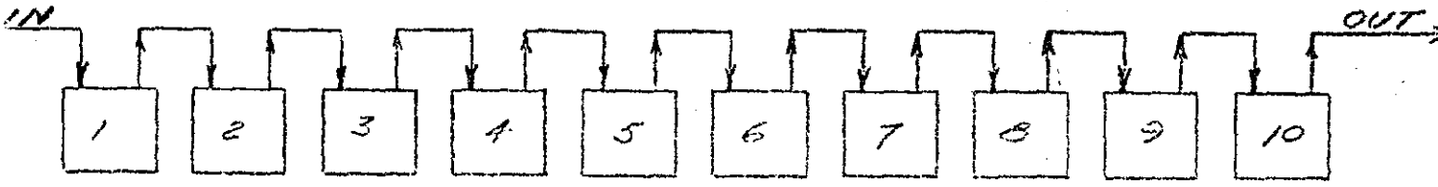
(0.75)(610) = 458 gallons.

Since ten vessels are employed the "batch-capacity" of the plant will be:

$$\frac{(10)(453)}{(4.25)(60)} = 17.9 \text{ g.p.m. of 80\% completion material.}$$

(b) If the design of each vessel is modified in accordance with Fig. 1, and (1) if the two available and modified units are hooked in series according to Fig. 6.

FIG.6



The theoretical circulating capacity, Q, of the propeller mixers is, from Nomograph I, 475 c.f.m. However at 60% efficiency, the actual circulating capacity will be:

$$(0.60)(475) = 285 \text{ c.f.m. or } 2130 \text{ g.p.m.}$$

The smallest length of time which a particle could spend in each vessel will be from equation (11).

$$t_m = \frac{(610)(0.1337)}{285} = 0.287 \text{ mins.}$$

The reaction velocity constant, k, for a second order reaction will be:-

$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

where:-

a = initial concentration of reactant A in mols /liter.

b = " " " " B " " ".

x = number of mols of A and B reacting in t minutes.

Therefore,

$$k = \frac{2.303}{180(10-5)} \log_{10} \frac{5(10-4)}{10(5-4)} = 0.001225$$

For a second order reaction;

$$\lambda = t_m k(a-b) = (0.237)(0.001225) = 0.00175 \text{ (See equation (17)}$$

The quantities p and q would be defined thusly:

$$p = \frac{R}{Q} = \frac{R}{295}$$

The desired mean completion, S, in the effluent from the given system would be given thusly:

$$S = \frac{b(a-x)}{a(b-x)} = \frac{5(10-4)}{10(5-4)} = 3$$

Since m = 10, from equation (25),

$$S = \left(\frac{pe^{\lambda}}{1-qe^{\lambda}} \right)^{m}$$

or,

$$3 = \left[\frac{\left(\frac{R}{295}\right)(e)^{0.00176}}{1 - \left(1 - \frac{R}{295}\right)\left(e\right)^{0.00176}} \right]^{10}$$

therefore,

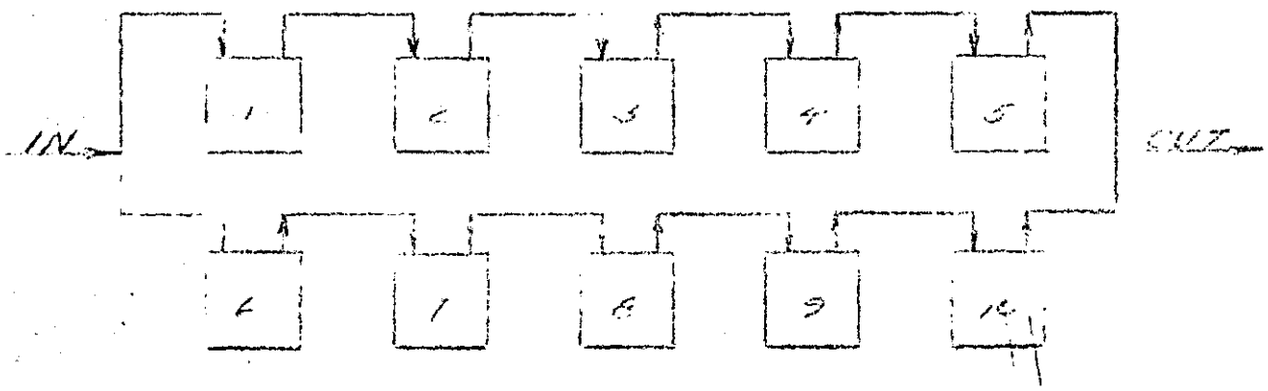
$$R = 4.9 \text{ c.f.m. } \underline{\text{or}} \text{ } 36.6 \text{ g.p.m.}$$

The percentage increase in plant capacity will be, therefore:

$$= \frac{36.6-17.9}{17.9} \times 100 = 104.5\%$$

(2) if the ten available and modified vessels are arranged as shown in Fig.(7

FIG.7



In this system m would equal 5, since the system would consist of two tandem of five vessels in series.

Hence,

$$S = \left[\frac{\left(\frac{R}{285}\right)\left(e\right)^{0.00176}}{1 - \left(\left(1-\frac{R}{285}\right)\left(e\right)^{0.00176}\right)}\right]^{5}$$

therefore,

$$R = 2.55 \text{ c.f.m. } \underline{\text{or}} \text{ } 19.05 \text{ g.p.m.}$$

The plant capacity will be:-

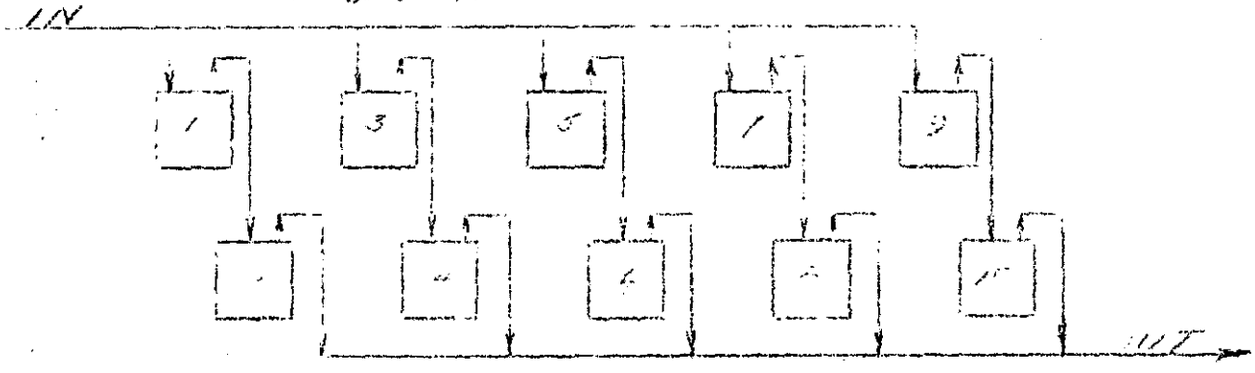
$$= (2)(19.05) = 38.1 \text{ g.p.m.}$$

The percentage increase in plant capacity will be, therefore:

$$= \frac{38.1 - 17.3}{17.9} \times 100 = 113\%$$

(3) if the ten available and modified vessels are arranged as shown in Fig. (8).

FIG.8



In this system m would equal 2, since the system would consist of five vessel tandems of two vessels in series:

Hence,

$$3 = \left[\frac{\left(\frac{R}{285}\right)\left(e\right)^{0.00176}}{1 - \left(1 - \frac{R}{285}\right)\left(e\right)^{0.00176}} \right]^2$$

therefore,

$$R = 1.88 \text{ c.f.m. or } 8.88 \text{ g.p.m.}$$

The plant capacity will be:

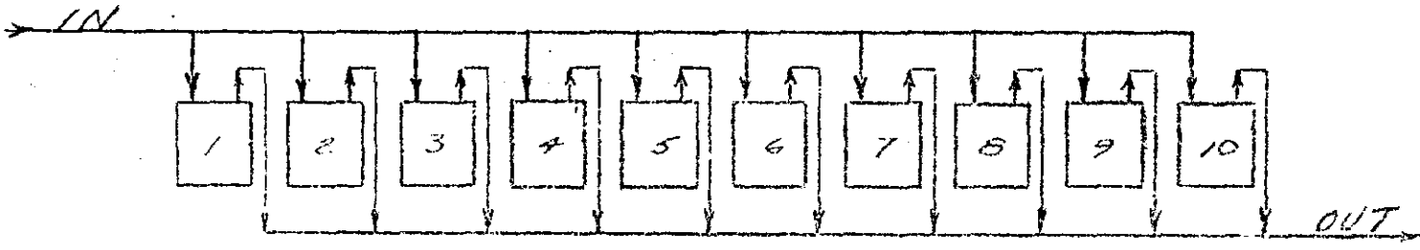
$$(5)(8.88) = 44.4 \text{ g.p.m.}$$

The percentage increase in plant capacity will be, therefore:

$$\frac{44.4 - 17.9}{17.9} \times 100 = 148\ \%$$

(4) if the ten available and modified vessels are arranged as shown in Fig. (9).

FIG. 9



In this system m would equal 1, since the system would consist of 10 vessels in parallel

Hence,

$$3 = \left[\frac{\left(\frac{R}{285}\right)\left(e\right)^{0.00176}}{1 - \left(1 - \frac{R}{285}\right)\left(e\right)^{0.00176}} \right]$$

Therefore,

$$R = 0.748 \text{ c.f.m. or } 5.58 \text{ g.p.m.}$$

The plant capacity will be:-

$$(10)(5.58) = 55.8 \text{ g.p.m.}$$

The percentage increase in plant capacity will be, therefore

$$\frac{55.8 - 17.9}{17.9} \times 100 = 212\%$$

(c)

(1) if the ten available and modified units are hooked in series according to Fig. (6), the following would obtain, where:

$R = 17.9$ g.p.m. $\qquad \lambda = 0.00176$

$Q = 2130$ g.p.m. $\qquad p = \frac{R}{Q} = \frac{17.9}{2130} = 0.0084$

$k = 0.001225$ $\qquad q = 1-p = 1-0.0084 = 0.9916$

$t_m = 0.237$ mins. $\qquad m = 10$

$$\frac{5(10-X)}{10(5-X)} = \left[\frac{(0.0084)(e)^{0.00176}}{1-(0.9916)(e)^{0.00176}}\right]^{10}$$

therefore,

$$X = 4.75 \text{ mols.}$$

The percent completion achieved for the thruput would be:

$$= \frac{4.75}{5.00} \times 100 = 95.0\%$$

(2) if the ten available and modified units are "hooked-up" according to Fig. (7), consisting of two tandem of five vessels in series, the following would obtain, where:-

$$R = \frac{17.9}{2} = 8.95$$

$$p = \frac{8.95}{2130} = 0.0042$$

$$q = 1 - 0.0042 = 0.9958$$

m = 5

$$\frac{5(10-\chi)}{10(5-\chi)} = \left[\frac{0.0047(e)^{0.00176}}{1-(0.9953)(e)^{0.00176}}\right]^5$$

therefore,

$$= 4.82 \text{ mols}$$

The percent completion achieved for the thruput would be:-

$$= \frac{4.82}{5} \times 100 = 96.4\%$$

(3) if the ten available and modified units are (hooked-up" according to Fig. (8), consisting of five tandems of two vessels in series, the following would obtain, where:

$$R = \frac{17.9}{5} = 3.55$$

$$p = \frac{3.55}{2130} = 0.001666$$

$$q = 1 - 0.001666 = 0.998334$$

$$m = 2$$

$$\frac{5(10-\chi)}{10(5-\chi)} = \left[\frac{(0.001666)(e)^{0.00176}}{1-(0.998334)(e)^{0.00176}}\right]^2$$

therefore,

$$\chi = 4.99 \text{ mols}$$

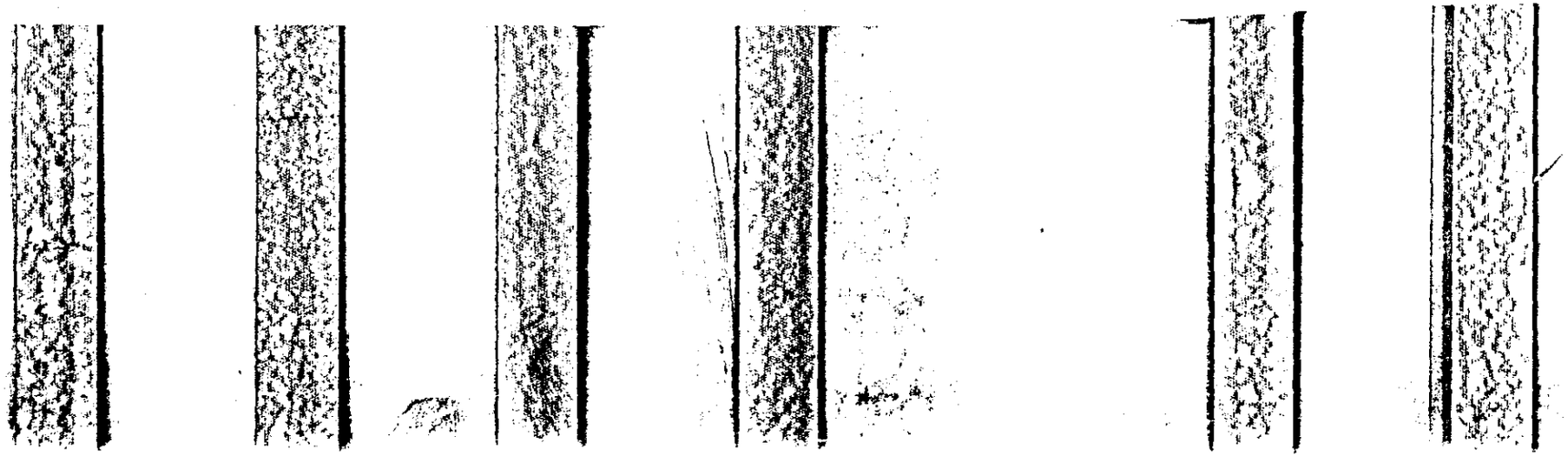
The percent completion achieved for the thruput would be:

$$= \frac{4.99}{5} \times 100 = 99.8\%$$

(4) if the ten available and modified vessels are arranged as shown in Fig. (9), consisting of ten vessels in parallel, the following would obtain, where:-

TABLE I

Hookup employed	Plant Capacity with 80% completion of reaction (G.P.M.)	Percent increase in capacity with 80% completion of reaction using continuous-operation instead of batch-operation.	Percent completion of reaction achieved with continuous operation and maintaining the plant batch operation capacity of 17.9 g.p.m.	The standard mean deviation from the mean holding time at throughput rates of 17.9 g.p.m. (Mean Holding Time = 340 Mins.)
10 vessels "batchwise"	17.9		80%	virtually = 0
10 vessels series	36.6	104.5%	95%	107.8
2 tandems of 5 vessels in series	38.1	113 %	96.4%	152.5
5 tandems of 2 vessels in series	44.4	148 %	99.8%	244
10 vessels in parallel	55.8	212 %	99.998%	340



$$R = \frac{17.9}{10} = 1.79$$

$$p = \frac{1.79}{2130} = 0.00084$$

$$q = 1 - 0.00084 = 0.99916$$

$$n = 1$$

$$\frac{5(10-\chi)}{10(5-\chi)} = \left[\frac{(0.00084)(e)^{0.00176}}{1 - (0.99916)(e)^{0.00176}}\right]$$

therefore,

$$\chi = 4.3999 \text{ mols}$$

The percent completion achieved for the thruput would be:

$$= \frac{4.9999}{5} = 99.998\%$$

For a tabulation of the results of the problem illustrated above, see Table I.

TABLE I

Hookup employed	Plant Capacity with 80% completion of reaction (G.P.M.)	Percent increase in capacity with 80% completion of reaction using continuous-operation instead of batch-operation.	Percent completion of reaction achieved with continuous operation and maintaining the plant batch operation capacity of 17.9 g.p.
10 vessels "batchwise"	17.9		80%
10 vessels series	36.6	104.5%	95%
2 tandems of 5 vessels in series	38.1	113 %	96.4%
5 tandems of 2 vessels in series	44.4	148 %	99.8%
10 vessels in parallel	55.8	212 %	99.998%

A study of the results in Table 7 is fruitful in developing an appreciation of the significance of the results and in developing thereby a means of selecting the optimum arrangement of the given equipment.

It is apparent that either of the two sets of measurements computed above may be used to estimate the comparative efficiency of each of the given arrangements. That is,

a. the completion of reaction characterizing the effluent in each arrangement under an identical throughput rate in each case

or,

b. the maximum throughput rate which may be employed in each arrangement to yield an identical completion of reaction in the effluent

constitute thoroughly interchangeable criteria of efficiency. Therefore, it should be noted that the remarks which are made below in explanation of the results shown in Column 3 of Table 7 reflect equally upon results in Column 1.

Brothman found that, for all values of numbers of vessels in series, the expression for the "standard mean deviation" from the mean holding-time equals $\frac{\sqrt{mc}}{p} t_m$. The values of the "standard mean deviation", computed accordingly, for the case of the identical throughput rate of 17.9 gpm are given in Column 4 of Table 7 . The fact that the extent of completion of the reaction, for the given case, tends to increase as the "standard mean deviation" increases gives the clue to the explanation of the results and provides us furthermore with a criterion for making the final selection of the arrangement to be used.

Drawing an analogy between the significance of the "standard mean deviation" from the mean holding-time in the case of continuous combining equipment and the role assumed by the "standard mean deviation" in the field of statistics, it may be observed that in both cases the greater the "standard mean deviation" from the mean the less efficient or "competent" is the mean in estimating any phenomenon or event which is related to the mean. Hence, where for the case of batchwise combining operations the "standard mean deviation" from a given holding-time is virtually zero, the holding-time within ~~("the mean holding-time")~~ the system precisely determines the completion of the combining phenomenon according to the statement that the completion of the combining phenomenon is a function of time. On the other hand, it stands to reason that where the "standard mean deviation" from the mean holding-time increases, the deviation as to completion (as referred to that which would be expected on the basis of the mean holding-time alone) should also increase. The deviation in the positive direction which characterizes the completions yielded upon increase in "the standard mean deviation" in the given example follows from (a) the logarithmic or exponential nature of the completion vs. time curve obtaining for the given combining phenomenon; and (b) the dispersion of significant values of P with respect to time obtaining each case.

Now, in what manner could the magnitude of the "standard mean deviation" from the mean holding-time conceivably affect the decision as to which arrangement should be used? To answer this question involves pressing home the fact that a large "standard mean deviation" from a mean indicates in our case a wide dispersion of significant values of P on both sides of the mean; while a small "standard mean deviation" from the mean indicates

a "bunching" or narrowing of the significant values of P within a limited band about the mean. In reactions ~~where~~ where, as in the cases of many organic syntheses, the prolonged sojourn of a reaction product within a system in contact with the reactants tends to promote side-reactions, arrangements involving large "standard mean deviations" would not be acceptable. Again, let us suppose that the reaction involved firstly the building up of a "chemical condensation" product or monomer, and secondarilly a polymerization. Furthermore, let us suppose that the object of the polymerization is a product having a special spatial structure and that the various polymerization operations are responsive to the quantitative relationships existing between the products of the various stages of the polymerization. In such an instance, the continuous system would have to guarantee not only a required completion with respect to the chemical condensation or monomer product but a minimum deviation in the affluent from a given mean holding-time. Therefore, the arrangement tending to limit the "standard mean deviation" to its minimum limits, namely the ten-in-series system would be virtually mandatory. As a matter of fact, it might well be that the goal of restricting the "standard mean deviation" ~~might well~~ would not only force the use of a ten-in-series arrangement but could furthermore make necessary a stepping-up of the rate of throughput at the expense of the obtained completion of reaction as a means of sharply restricting the "standard mean deviation".

In this connection, it might be well to point out that Brothman's work has indicated that approximations as to the precise proportions of materials passing from a continuous combining system within set deviations from the mean holding-time may be obtained by the use of well-known ~~theories~~ theorems taken from the field of mathematical probability. A useful theorem in this

connection is that of Bienayme - Tchebycheff. The proper coordination of such theorems with the mathematics used to derive the basic formulae used here is good and proper since the branch of mathematics used here is isomorphic with the field of mathematical probability.

There are, of course, other considerations which might influence the decision as to which arrangement should be used. Those might include:- (a) the complexity of the piping and control system required to assure a uniform rate and quality of feed to a parallel system involving a large number of units; (b) the capacity of the equipment comprising the subsequent stages of a continuous hookup; (c) the economical considerations involved; etc. In a word, the designing of continuous plants involves the consideration and skillful interpenetration of a host of factors, many of which may be peculiar to the particular problem at hand.

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FIG. 1: A HIGH EFFICIENCY CONTINUOUS MIXING VESSEL

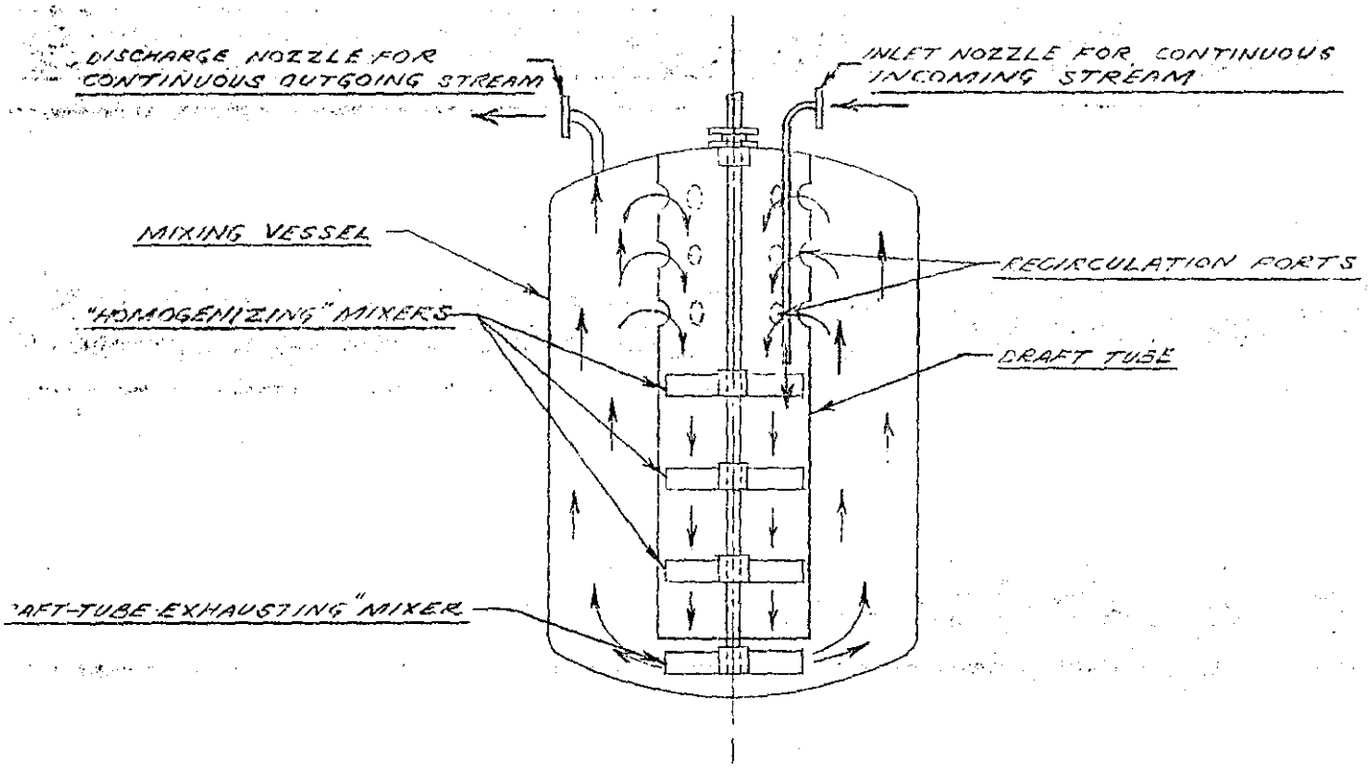
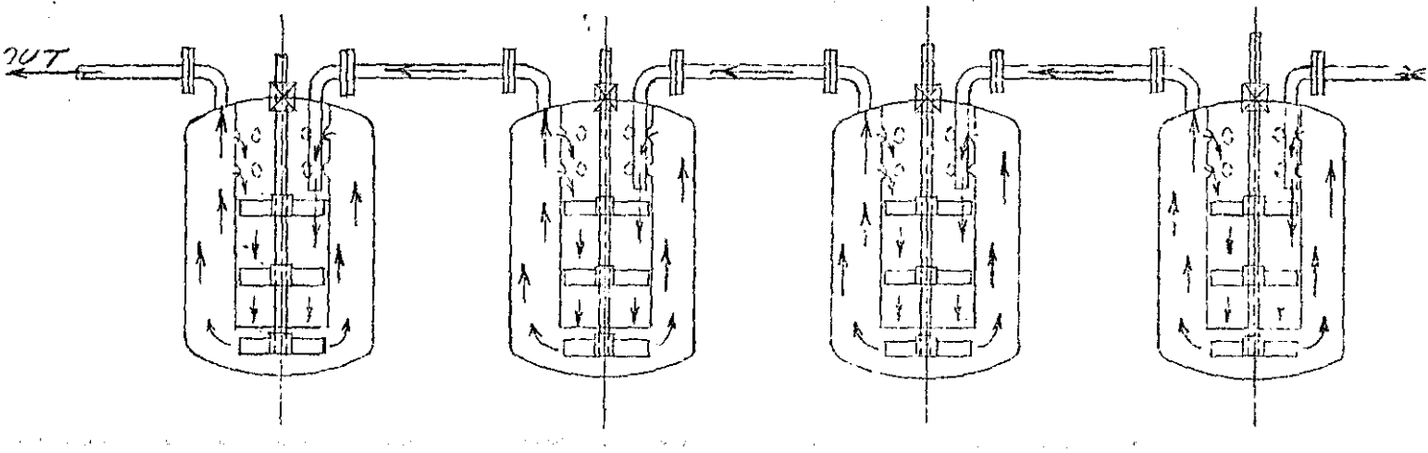
FIG. 2: A CONTINUOUS COMBINING SYSTEM COMPRISING A SERIES OF VESSELS