

UNCLASSIFIED

1
AECU-3247

ENGINEERING

UNITED STATES ATOMIC ENERGY COMMISSION

THE FLUIDIZED CONDENSER (thesis)

By
Curt B. Beck
Thomas D. Canby
Irwin S. Zonis

May 10, 1952

Engineering Practice School
Massachusetts Institute of Technology
Oak Ridge, Tennessee



Technical Information Service Extension, Oak Ridge, Tenn.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Other issues of this report may bear the number KT-123.

Work performed under Contract Number W-7405-Eng-26, Sub-contract 70 for K-25 Plant, Carbide and Carbon Chemicals Division, Oak Ridge, Tennessee.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA. Price 45 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AECU-3247

THE FLUIDIZED CONDENSER

by

Curt B. Beck

Thomas D. Canby

Irwin S. Zonis

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

from the

Massachusetts Institute of Technology

1952

ACKNOWLEDGEMENTS

The authors wish to express their gratitude for the assistance given them by Professor T. H. Pigford of the Massachusetts Institute of Technology Engineering Practice School, and by the personnel of the Carbide and Carbon Chemicals Company, especially Mr. G. A. Strasser, Mr. J. Ramsey, Mr. W. Whitson, and Mr. J. Williams.

The authors also wish to express appreciation to the United States Atomic Energy Commission and to the Carbide and Carbon Chemicals Company, through whom the facilities were made available.

THE FLUIDIZED CONDENSER

Submitted by Curt B. Beck, Thomas D. Canby, and Irwin S. Zonis on May 10, 1952, in partial fulfillment of the requirements for the degree of Master of Science at the Massachusetts Institute of Technology.

ABSTRACT

An apparatus using a fluidized bed of cold, recycled zirconium-tetrachloride powder to condense a stream of hot zirconium-tetrachloride vapor was designed and constructed. The operation of the fluidized condenser was successfully demonstrated. It was shown that caking of zirconium tetrachloride on the walls of the column was slight, with the greatest part of the condensation occurring in the fluidized phase. Because of time limitations, few runs were made.

Data from future experimental runs on the fluidized condenser may be used in a proposed theoretical analysis, in which several equations have been developed to allow the design of a fluidized condenser for given operating conditions. These equations predict optimum column size for the desired degree of condensation, axial temperature gradient in the bed, and overall heat-transfer and mass-transfer coefficients.

TABLE OF CONTENTS

I.	SUMMARY.	8
II.	INTRODUCTION	10
III.	APPARATUS.	12
IV.	PROCEDURE.	13
V.	RESULTS AND DISCUSSION	
	A. Experimental Results.	15
	B. Theoretical Analysis.	17
VI.	CONCLUSIONS.	21
VII.	RECOMMENDATIONS.	22
VIII.	APPENDIX	
	A. Detailed Operating Procedure.	23
	B. Details of Apparatus.	27

TABLE OF CONTENTS (Cont'd)

C. Design of Apparatus	32
Legend for Figure 1.	34
D. Theoretical Analysis	39
1. Properties of the Bed.	39
2. Heat and Mass Transfer in Fluid-Solid Systems.	41
3. Superheated Gas Mixtures	44
4. Saturated Gas Mixtures	48
5. Recycle Rate	53
6. Overall Coefficients	53
7. Literature Values for Exponents and Coefficient.	54
E. Sample Condenser Design.	55
F. Experimental Data.	59
G. Nomenclature	73
H. Literature Citations	78

I. SUMMARY

It was the purpose of this work to design an apparatus for the condensation of zirconium-tetrachloride vapor from an inert gas stream. The apparatus was to be designed for use in a continuous process, and no mechanical aids, such as scrapers or doctor knives, were to be used, since the purity of the product might be diminished. A condenser was designed, utilizing a fluidized bed of zirconium-tetrachloride powder to condense the tetrachloride vapor. A recycle of cooled zirconium-tetrachloride powder accomplished condensation and minimized caking of tetrachloride on the walls.

The apparatus consisted of a sublimer, a metering section, a diluent preheater, a recycle cooler, and a fluidized bed. A sublimer was used to provide zirconium-tetrachloride vapor, which was metered by measuring the pressure drop of the vapor as it passed through a capillary tube. The pure tetrachloride vapor was diluted to the desired concentration by mixing with preheated nitrogen. The mixture was passed through heated lines to the fluidized condenser where the entering gas stream caused fluidization of a bed of relatively cool tetrachloride powder. A fraction of this powder was removed continuously from the bed, and was carried by a pneumatic lift through a heat exchanger into a holdup bin, from which part of the powder was dumped into a product receiver. The rest was returned to the column to act as fresh heat-exchange surface.

The authors succeeded in demonstrating the successful operation of the fluidized bed in condensing zirconium tetrachloride. Only a slight amount of caking on the walls occurred, and with the greater part of the condensation taking place in the fluidized bed itself, the product was conveniently withdrawn as powder.

Data from future experimental runs may be used to determine experimentally the optimum values for the empirical coefficients and exponents of the

proposed theoretical analysis, in which several equations have been developed to permit design of a fluidized condenser for given operating conditions. The first design equation relates properties of the gas mixture to properties of the mixture at the point at which saturation is reached. The nomenclature may be found in the Appendix, Section G.

$$\ln\left(\frac{T_s - T_b}{T_1 - T_b}\right) = \int_{Y_1}^{Y_s} \frac{dY}{(N_{Le})^m (1 + Y) \ln(1 + Y)}$$

The next equation yields the height of bed necessary to reach saturation. In this section of the bed, the gas stream is unsaturated (i.e., superheated).

$$L_s = - \int_{Y_1}^{Y_s} (F)(D_p)(Q)^n (N_{Re})^f (N_{Sc})^m \left[\frac{dY}{(1 + Y) \ln(1 + Y)} \right]$$

The next equation determines the height of bed from the point where saturation is reached to the point where the desired degree of condensation is attained.

$$L_2 - L_s = - \int_{T_s}^{T_2} (F)(D_p)(Q)^n (N_{Re})^f (N_{Pr})^m \left[\frac{1 + \frac{a_1}{a_2}}{T - T_b + a_1} \right] (dT)$$

In addition, supplementary equations permit calculation of:

1. temperature gradient in each section of the bed,
2. recycle rate for any given bed temperature and feed,
3. amount of material condensing on recycled solids compared to the amount condensing as a mist in the fluidized phase, and
4. overall heat-transfer and mass-transfer coefficients.

II. INTRODUCTION

Sublimation is a unit operation about which little material has been published, since there is a limited number of commercially important compounds, such as iodine, uranium hexafluoride, and zirconium tetrachloride, which undergo sublimation under industrially important conditions. In a recent paper, Nord (30) sums up the standard formulae which may be used in making sublimation calculations, and points out the lack of any design equations for use in condensers following sublimation operations. These condensers usually consist of some form of cooled surface (20) with provisions made for removing the condensed solids mechanically. Little is known about heat-transfer rates in such systems; and design must be empirical.

In one method of production of zirconium tetrachloride it is necessary to remove this compound from a gaseous mixture containing approximately one-third zirconium tetrachloride and two-thirds non-condensables. It would be preferable to remove the tetrachloride continuously. Since the triple point of zirconium tetrachloride is 437°C and 18.7 atm. absolute pressure, it is impractical to condense the tetrachloride as a liquid. Moreover, it is undesirable to use condensation on a cool surface with subsequent removal of the product by a mechanical scraper, since contamination might result which could render the zirconium unfit as a structural material in nuclear reactors. A batchwise condensation (i.e., condensation in a cooled receptacle followed by removal of the solid) has been proved inefficient (34) and has been shown to result in partial decomposition of the zirconium tetrachloride from contact with water vapor and oxygen during the removal operation.

A new type of condenser has been suggested for this operation which would be suitable for other materials as well as for zirconium tetrachloride. This condenser would utilize a fluidized bed of recirculated and cooled

zirconium-tetrachloride solid to condense the hot vapors. Nucleation and condensation should be rapid in such a system since a large surface area for condensation would be provided by the fluidized particles. Preliminary column design could be determined from the equations developed by Miller and Logwinuk (26), who express critical mass velocity for a fluidized bed in terms of properties of the system. Various formulae are available for calculating heat transfer to fluidized particles (12, 18, 25), and there is some valuable work devoted to the theory of heat and mass transfer in batch condensation of solids in a closed chamber (4). It would be advantageous to apply the available theories to derive design equations to supplement experimental work.

It was the purpose of this investigation to demonstrate the feasibility of using a fluidized condenser for the continuous condensation of zirconium tetrachloride, and, if possible, to develop design generalizations as applied to fluidized condensers. A pilot-scale fluidized condenser was to be constructed and its operation tested when supplied with a metered mixture of gaseous zirconium tetrachloride and nitrogen.

III. APPARATUS

The apparatus (see Figure 1, Appendix C) consists of a sublimator to provide zirconium-tetrachloride vapor, a capillary-tube metering section to meter the hot vapor, a nitrogen preheater to provide hot inert diluent, and the column, which contains the fluidized bed. The motor-driven star valve removes a portion of the bed continuously, and the pneumatic-transport system carries this powder through the heat exchanger into the holdup bin. Some powder is withdrawn as product and the rest returned to the column through suitable valves. The exit gas from the column is sampled by an electrostatic precipitator.

IV. PROCEDURE

After fresh zirconium tetrachloride has been added both to the column to form the initial bed for fluidizing and to the sublimator to provide material for vaporization when required, and after all lines have been checked to be certain that they are free of plugging, the lines and metering section are brought up to the operating temperature, approximately 400°C, to prevent premature condensation of the tetrachloride.

Power is supplied to the preheater to bring the diluent nitrogen to the desired temperature, about 380°C. The sublimator is then heated to about 340°C, or to the temperature at which the desired flow of tetrachloride vapor is achieved. The vapor flow rate is indicated by a manometer connected to a capillary constriction. Preliminary flow of tetrachloride is bypassed to an exhaust line instead of being sent to the condenser.

When the run is started, the star valve and pneumatic lift are turned on, and diluted zirconium-tetrachloride vapor is sent to the fluidized condenser rather than being bypassed. Wall temperatures of the condenser are recorded, as are other temperatures indicated on the diagram of the apparatus (Figure 1). Also measured and recorded are:

1. the several static pressures and differential pressures for the column, the pneumatic lift, and the capillary-tube metering section;
2. the flow of cooling water to the heat exchanger of the pneumatic lift; and
3. the rate of diluent feed and purge nitrogen used to prevent plugging of the manometer taps.

The recycle rate is altered by changing the speed of rotation of the star valve, which is of known volumetric capacity, and the rate may be checked by observing change in level of the recycle receiver. Product withdrawal

rate is controlled by the plug valve above the product-receiver bin. The exit gas stream is analyzed for solids content by the use of an electrostatic sampling precipitator.

The apparatus is shut down by bypassing the tetrachloride vapor through an exhaust line, shutting off the vaporizer, cooling the lines, and stopping the recycle of cooled solids. Purge nitrogen is not stopped until it is certain that no chance exists for plugging in any of the manometer taps.

V. RESULTS AND DISCUSSION

A fluidized condenser has been successfully operated, using a bed of fluidized zirconium-tetrachloride powder to condense a dilute stream of zirconium-tetrachloride vapor.

A. EXPERIMENTAL RESULTS

The most desirable characteristic of a fluidized condenser would be the condensation of vapors in the fluidized phase to form a powdered product which would facilitate continuous operation. It was anticipated that condensation on the walls would cause some caking there and would prevent successful operation.

When the fluidized condenser was operated as a batch unit, i.e., with no removal of hot bed material nor addition of cooled recycle solids, caking of zirconium tetrachloride on the walls of the column was rapid. The cross-sectional area of the fluidized bed at the entrance of the gas stream was reduced approximately 90% in about 100 minutes of operation. This restriction in the lower part of the column caused the fluidized bed to climb; caking on the walls likewise progressed up the column, so that when the run was terminated, a thick hard cake existed practically throughout the column. It became obvious that batch operation of the fluidized condenser with sole cooling by heat transfer through the walls would not yield the desired results.

The fluidized condenser was then operated as a continuous unit. Because of difficulties encountered in the operation of the recycle system, it was found necessary to simulate continuous recycle by the manual introduction of cold zirconium-tetrachloride powder to the recycle holdup bin,

and manual withdrawal of an equivalent amount of bed material from the bottom of the column. Under these conditions, caking was held to a negligible amount, the tetrachloride was condensed in the fluidized phase so that it could be withdrawn from the column easily, and the condenser was operated successfully for 40 minutes. The run was terminated only because of depletion of material in the sublimator; had more feed been available, the condenser could probably have been operated for a much longer period of time.

Little data were taken in this work which might be used in the proposed theoretical analysis. Temperature traverses were not completed, and insufficient data were obtained for material balance calculations.

A small column with insulated walls could easily replace for laboratory study the large column used in this work. Material would be conserved, ease of operation might well be increased, and smaller equipment would allow easier simulation of apparatus such as the recycle system. Close attention would have to be paid to the influence of wall effects on the overall condensation picture.

Improvements to the present apparatus are suggested in the Appendix, Section B.

B. THEORETICAL ANALYSIS

By consideration of simultaneous heat transfer and mass transfer in a fluidized bed, it was possible to develop a theoretical analysis which allows the design of a fluidized condenser, and the calculation in advance of the conditions which would exist during a run. In order to allow the use of the equations, a knowledge of the entrance conditions and of the properties of the inert gas and the condensable vapor must be postulated.

It is probable that the dilute tetrachloride-inert mixture will enter the condenser as a superheated stream. The first equation allows determination of the concentration and the corresponding temperature at which saturation will be reached.

$$\ln\left(\frac{T_s - T_b}{T_1 - T_b}\right) = \int_{Y_1}^{Y_s} \frac{dY}{(N_{Le})^m (1 + Y) \ln(1 + Y)}$$

In this equation, (T_1) is the entrance temperature of the gas mixture, (T_b) is the bed temperature, and (T_s) is the temperature at which saturation is reached. The entrance concentration is (Y_1) , and (Y_s) corresponds to (T_s) . The Lewis number (N_{Le}) is the ratio of the Prandtl number of the gas mixture to the Schmidt number of the gas mixture. The exponent (m) is an empirical quantity.

The second equation predicts the height of bed necessary for the gas stream to reach saturation.

$$L_s = - \int_{Y_1}^{Y_s} (F)(D_p)(Q)^n (N_{Re})^f (N_{Sc})^m \left[\frac{dY}{(1 + Y) \ln(1 + Y)} \right]$$

In the above equation, (F) is an empirical coefficient, (D_p) is the particle size, and (Q) is the ratio of the actual particle density to the apparent bed density. The exponents (n) and (f) are empirical quantities. The bed height at which saturation is reached is (L_s), (N_{Sc}) is the Schmidt number of the gas mixture, and (N_{Re}) is a modified Reynolds number of the gas mixture,

$$(N_{Re}) = \frac{(D_p)(V)(M)(1 + Y)}{(A_t)(\mu)}$$

Here (V) is the inert molar feed rate, (M) is the molecular weight of the gas mixture, (A_t) is the cross-sectional area of the column, and (μ) is the viscosity of the gas mixture.

The next equation yields the height of bed from the point where saturation is first reached to the point at which the desired degree of condensation is reached.

$$L_2 - L_s = - \int_{T_s}^{T_2} (F)(D_p)(Q)^n (N_{Re})^f (N_{Pr})^m \left[\frac{1 + \frac{a_1}{a_2}}{T - T_b + a_1} \right] dT$$

Here (N_{Pr}) is the Prandtl number of the gas mixture, (T_2) refers to the exit temperature of the gas mixture as it leaves the bed, and (a_1) and (a_2) are functions of the nature of the gas mixture and the concentration of the mixture,

$$a_1 = \left(\frac{\lambda}{MC} \right) (N_{Le})^m \ln(1 + Y)$$

$$a_2 = \left(\frac{RT^2}{\lambda Y} \right) (N_{Le})^m \ln(1 + Y)$$

In the above equation, (C) is the specific heat of the gas mixture, (λ) is the latent heat of the condensable vapor, and (R) is the gas constant.

These equations allow prediction of the temperature gradient in the bed, and of the physical dimensions of the bed necessary to effect adequate condensation. From these equations and the supplementary equations developed in the Appendix, it is possible to calculate overall heat-transfer and mass-transfer coefficients.

$$h_o = \frac{(C_r)(r)(T_b - T_r)}{(S_b)(L_2)(T_1 - T_2)} \ln \frac{T_1 - T_b}{T_2 - T_b}$$

$$K_o = \frac{(V)(1 + Y_1)(1 + Y_2)}{(S_b)(L_2)(P)} \ln \frac{(Y_1)(1 + Y_2)}{(Y_2)(1 + Y_1)}$$

In these equations, (h_o) and (K_o) are the overall heat-transfer and mass-transfer coefficients respectively, (C_r) is the specific heat of the recycled solids, (r) is the recycle rate of the cooled solids, (S_b) is the average surface area of all the particles in a unit height of bed, and (T_r) is the temperature of the cooled recycled solids as they enter the column. The total height of the bed is (L_2), (Y_2) is the exit concentration of the gas mixture as it leaves the bed, and (P) is the total pressure in the column.

Preliminary values of the empirical exponents and coefficient may be obtained from the literature.

(F) = 0.114	Gamson, (12)
(f) = 0.41	<u>Ibid.</u>
(n) = 1.61	<u>Ibid.</u>
(m) = 2/3	Chilton and Colburn (6).

A sample calculation, using the proposed theoretical analysis and values for the empirical quantities taken from the literature, yielded the following results.

The feed was 1.0 mole/hr. of zirconium tetrachloride, and 2.0 mole/hr. of nitrogen, entering the column at 450°C. With a bed temperature of 120°C, a recycle rate of 2800 lb./hr., and an exit concentration of 1.0 mole of tetrachloride lost for every 5000 moles entering the column as vapor (i.e., 99.98% condensation), a bed height of 17-1/2 in. in a 3-in. diameter column is sufficient. For this case, the overall heat-transfer coefficient is 740 B.t.u./(hr.)(sq. ft.)(°F), and the overall mass-transfer coefficient is 39.4 (lb.-moles)/(hr.)(sq. ft.)(atm.).

The equations of the theoretical analysis are developed in full in the Appendix. It is suggested that sufficient data be taken on the fluidized condenser so that values of the empirical coefficient and exponents may be determined for the case of the fluidized condenser. In addition, the bed-density factor (Q) could be determined experimentally. The literature values for these terms are satisfactory for preliminary evaluation, but it would be highly desirable to use the forms of the theoretical analysis presented here and the experimentally-determined coefficient, factor, and exponents for the design of another fluidized condenser.

VI. CONCLUSIONS

1. A condenser using a fluidized bed of zirconium tetrachloride to condense a dilute stream of zirconium-tetrachloride vapor has been operated successfully to produce a satisfactory product. Condensation is accomplished by recycle of the bed material and external cooling of the recycle.
2. An apparatus has been constructed to yield a stream of vaporized zirconium tetrachloride, to meter this vapor, and to dilute this vapor to any desired concentration with an inert gas. The metering section has yielded a satisfactory calibration curve.
3. Equations have been developed to design and predict the operation of a fluidized condenser. These equations yield the physical dimensions of the column as well as the overall heat-transfer and mass-transfer coefficients.

VII. RECOMMENDATIONS

1. It is recommended that further experimental work be performed on the fluidized condenser in order to amass sufficient data to test the efficacy of the proposed theoretical analysis and to evaluate the empirical quantities of the theoretical analysis.
2. It is suggested that several modifications to the fluidized-condenser system be undertaken:
 - a. A stainless-steel or nickel rotameter to replace the metering section now in use, or development of an entraining sublimers, using nitrogen or argon as the entraining medium,
 - b. Direct-resistance heating of the preheater, to replace the Calrod units now in use,
 - c. Direct-resistance heating of the line from the sublimers to the condenser,
 - d. Improvement of the recycle system, with substitution of a commercial injector or eductor and a gas-tight, efficient star valve,
 - e. The use of argon or helium instead of nitrogen, since zirconium may be contaminated by nitrogen used in its manufacture,
 - f. The substitution of a small column for the larger column now in use,
 - g. Inclusion of appropriate safety equipment, and
 - h. Instrumentation of the system to the extent of an automatically-controlled throttling valve below the metering section to hold the condensable-vapor flow rate constant.
3. It is recommended that additional theoretical work be performed to improve the analysis. In particular, a theoretical approach to the problems of mean particle size in the bed and apparent bed density would be highly desirable.

VIII. APPENDIX

A. DETAILED OPERATING PROCEDURE

The first step in the operation of the fluidized condenser is the checking of all lines to eliminate any plugging. The outlet of the bypass line is checked to ascertain that it is free of a plug of zirconium oxychloride, which results from the reaction of zirconium tetrachloride and water vapor. A plug may be cleared by drilling with a small bit. The manometer taps (P-3, P-4) are now tested for plugging. By closing the small glass stopcocks (V-14, V-15) connected to the static and differential manometers of the metering section, these manometers are closed off, and blowing is prevented. The midget valves (V-11, V-12) on the manometer-tap purge lines are then opened, and a large volume of nitrogen is blown into the taps. After a minute of the high flow rate, the purge is throttled to the desired flow, as indicated by the small purge-nitrogen rotameters (R-1, R-2). A flow of approximately 2600 cu. cm./min. has been found to be suitable, preventing plugging and yet not interfering with accurate metering.

The glass stopcocks to the manometers are now opened cautiously. An unusual differential or static pressure indicates plugging of the taps of the metering capillary. The taps and capillary may be cleaned with a stiff wire or a stream of high pressure air. Care should be taken to prevent blowing of the manometers, since no traps have been used on the metering-section manometers (see Discussion of Apparatus). Under conditions of no plugging, the differential should be zero with the desired amount of purge nitrogen flowing through each tap.

The next step in the operation of the condenser is to fill the clean, dry sublimator with fresh zirconium tetrachloride. One filling of the sublimator should be adequate for two runs of 60 to 90 minutes each. The neck of the sublimator should next be filled with a porous plug of glass wool to filter out any dust which might be carried into the metering section by the vapor

stream. A small section of stainless-steel screen is used between the neck of the sublimer and the metering section to prevent the glass wool from being forced into the metering section. This screen is secured by two recessed asbestos gaskets between the flanges of the sublimer and the metering section.

The sublimer is then bolted to the metering section. The tetrachloride throttling valve (V-1) is opened to a midway position, the bypass valve (V-2) is opened, and the flexible rubber exhaust tube is placed in position so that tetrachloride vapor from the bypass line will be carried away. The valve (V-13) to the condenser is shut. At the discretion of the operating group, tetrachloride may be vented into the plant's exhaust ducts by the large-diameter flexible hose, or a water-jacketed horizontal batch condenser may be used as a bypass. During this work the water-cooled apparatus was used for calibration of the metering section, while the flexible hose was used as bypass for fluidized-condensation runs.

The temperature-recording controller (T.R.C.) regulating power to the metering-section clamshell heater (F-2) is now turned on, and the temperature is set for 425°C . Meanwhile, the skin temperature of the preheater is raised to about 780°C by powerstats (H-3, H-4), and the manometer taps (H-1, H-2) are raised to 400°C . Also, the smaller powerstats are turned on to heat the lines to about 400°C (Z-1, Z-2, Z-3, Z-4). The large glass stop-cock (V-6) on the top recycle line is opened, the vibrator (B-3) on this line is turned on, bubbler nitrogen is passed into the condenser pressure taps (P-1, P-2), and tetrachloride is added to the column from the holdup bin (K-1) atop the recycle line. Fresh feed may be added to the column through the bin (K-1). The bed is brought to the desired height, i.e., about 2 ft. above the gas inlet.

Bubbler nitrogen is passed into the cone below the star valve (D), the pneumatic lift (V-5, R-3) and the vibrators (B-1, B-2) are turned on, and the star valve is rotated by the drive motor. Zirconium-tetrachloride powder should be carried up and cooled as it passes through the water-

jacketed heat exchanger. If the lift operates satisfactorily, it may be turned off to await later use.

With the desired bed height in the condenser, and all lines unstopped and brought up to temperature, the preheater nitrogen (V-3, V-4, R-4, R-5) may be turned on. This gas stream, used to dilute to the desired concentration the pure zirconium-tetrachloride vapor from the sublimator, soon reaches an operating temperature of about 380°C . The bed should fluidize satisfactorily.

The temperature-recording controller (T.R.C.) for the sublimator clamshell (F-1) may now be turned on and the temperature of the contents brought up to about 340°C . As the temperature of the sublimator rises, tetrachloride is vaporized at an increasing rate and passes out the bypass line. The flow may now be throttled down (V-1) to increase the static pressure (M-2) to about 8 in. Hg, and then may be adjusted to a desired flow of tetrachloride.

When the desired flow is obtained, the valve (V-13) to the condenser is opened and the bypass valve (V-2) is shut. Note that valve (V-13) must be opened before the bypass valve (V-2) is closed, or zirconium tetrachloride will be forced up into the manometer taps and manometers, plugging them severely. Tetrachloride vapor is now passed into the condenser. With the proper upstream static pressure, the metering-section differential pressure may be maintained constant.

The pneumatic-lift recycle line is now started to supply cooled solids to the fluidized bed. Product may be withdrawn into the product receiver (G) at a rate equal to the feed rate of tetrachloride vapor. During the run, temperatures of the bed, gas, and wall should be recorded, as should the pressure drop through the bed and the static and differential pressures at the metering section.

The exit concentration of the gas stream may be determined by means of an electrostatic sampling precipitator (J) which causes the precipitation and

collection of any dust particles from the cool gas stream by means of an induced electrostatic field. The collecting tube of the precipitator may be weighed to determine the amount of dust collected.

When the run has proceeded for a sufficient length of time (60 to 90 minutes), the apparatus may be shut down. The first step is to close the glass stopcocks (V-14, V-15) connected to the metering-section manometers to prevent blowout of the manometers. Next the bypass valve (V-2) is opened and valve (V-13) is shut. The sublimator clamshell (F-1) should then be shut off and opened to the air to cool the sublimator quickly, to prevent excessive loss of zirconium tetrachloride.

After the sublimator bed has dropped to a reasonably low temperature (200°C) so that little tetrachloride is being vaporized, the power input to the metering-section heater and the tap heater may be shut off, and the section allowed to cool slowly. When the temperature of the metering section has dropped to about 200°C , the nitrogen purge to the manometer taps may be shut off.

The product withdrawal should have been at a proper rate so that the tetrachloride holdup in the bed was constant. However, to check, the powder may be removed from the condenser, holdup bin, and recycle lines, and may be weighed to complete a mass balance.

The preheater nitrogen, having been allowed to flow to purge the lines of any remaining zirconium tetrachloride, may next be shut off and the power to the preheater cut off. The serpentine heaters (Z-1, etc.) may be allowed to cool, and purge nitrogen through all pressure taps may be shut off. During shutdown, the bypass line should be examined frequently to clear away any signs of plugging.

B. DETAILS OF APPARATUS

A major problem encountered in this work was the production of a metered quantity of zirconium-tetrachloride vapor which could be diluted with a measured amount of hot inert diluent, in this case nitrogen gas. It was decided to use a sublimator and a metering section to provide the measured flow of vapor, and, as a separate unit, a preheater to supply hot diluent at a predetermined rate. The diluent would be mixed with the vapor just before the mixture entered the condenser.

The sublimator first used was fabricated from 4-in. double-tough Pyrex pipe, which failed to withstand thermal stress. A metal sublimator was then built of a 4-in. nickel tube, with flanges and thermocouple wells silver-soldered to the tube, which operated satisfactorily for several calibration runs. Replacement was required when the silver solder deteriorated under the combined influence of tetrachloride and high temperatures.

An all-welded sublimator was fabricated from 5-in. nickel tubing. The sublimator gave excellent service, withstanding temperatures as high as 1000°C when empty.

An optimum diameter of 1/8-in. was calculated for the capillary tube to be used in the metering section. A stainless-steel metering section was fabricated of two 1-in. I.D. calming sections 5 in. long, silver soldered to a 1/8-in. O.D. capillary tube 1-1/2 in. long. The whole was heated with Nichrome wire. Again the silver solder corroded rapidly, and the Nichrome was unreliable for heating to the required temperature.

A second metering section was constructed of the same dimensions, but was welded by a Heliarc process. A clamshell-type muffle furnace replaced the Nichrome heaters. When combined with the differential-pressure measuring system described below, the metering section functioned in a completely satisfactory manner. By raising the temperature of the sublimator, a static

pressure of 6 to 8 in. Hg could be maintained before the capillary of the metering section, and the desired differential and flow rate could be obtained without difficulty by adjusting the throttling valve after the metering section. The calibration curve for the metering section is included in the report.

The pressure drop across the capillary tube of the metering section and the static pressure upstream of the capillary tube were measured by means of liquid-filled manometers. Several modifications of the initial equipment were necessary before the metering section could be made to operate successfully without plugging in the pressure taps because of condensation of zirconium tetrachloride.

Short Nichrome-heated sections of tubing leading from the taps to the manometer lines, with a few hundred cubic centimeters per minute of purge nitrogen fed to each tap from sight-feed bubblers, proved ineffective because of diffusion and surging of zirconium tetrachloride from the metering section into the taps. Plugging occurred even though the taps themselves were held at 400°C; condensation took place in the cooler tubing above the heated section.

The heated sections of the taps were then extended so that each tap had over 3 ft. of heated tubing between the metering section and the cool manometer lines. In addition, the purge-nitrogen rate was increased by a factor of ten. Again plugging occurred at the first cool section of tap line, even though the tap temperature was 600°C, and the purge rate was increased to about 2500 cu. cm./min. for each tap.

Satisfactory operation of the pressure taps was achieved only when the tap temperature was held at slightly over 400°C, the high purge rate was maintained, and the manometers were removed from the instrument panel and placed immediately adjacent to the metering section. No manometer traps were used. In this manner, the volume available for surging was kept to a minimum,

and the diffusion rate of the tetrachloride was kept low by the lowered tap temperature.

This technique allowed continued successful operation of the metering section, and the desired flow rate of zirconium tetrachloride could be obtained by means of the needle throttling valve immediately downstream of the metering section. It should be pointed out that points of preliminary calibration made with only a small amount of purge nitrogen do not deviate significantly from points of later calibration runs, which used a much higher amount of purge nitrogen.

Calibration of the metering section was accomplished by condensing and collecting in a tared, horizontal water-cooled glass condenser the zirconium-tetrachloride vapor produced and metered in a given length of time.

The inert gas used to dilute the pure tetrachloride vapor from the sublimator and metering section to the required concentration for the fluidized condenser was brought to the required temperature by means of a nitrogen preheater. This preheater, two units in series, was constructed of a Calrod heater in the center of a long tube of slightly greater inside diameter than the outside diameter of the Calrod. One end of the Calrod was fixed, while the other, supported by spacers, was free to expand and contract. Thus thermal expansion of the tube or the Calrod could not cause fracture of the heating element. Nitrogen was passed through the annular space, and the exit temperature of the gas could be held at the desired high level with only a slight pressure drop in the preheater.

The first method of attack on the problem of production of dilute zirconium tetrachloride was the use of an "entrainer" in which a heated stream of nitrogen was passed through a bed of heated zirconium tetrachloride. No correlation could be found between concentration of zirconium tetrachloride in the mixture and the indicated temperature of the bed. The entrainer

was therefore abandoned as a method of producing a known tetrachloride-nitrogen mixture. However, an entrainer is inherently simpler in operation than the metering system described above. It is suggested that an entrainer might be made to operate successfully if the bed were agitated or fluidized to allow the bed to reach a uniform temperature.

Several types of heating units were employed in the system. The sublimator was heated by a 7500-watt, 250-volt muffle furnace, and the metering section by a 1750-watt, 230-volt muffle. Each furnace was of the clamshell type.

The manometer taps were heated by lengths of Calrod. These rod-shaped elements, consisting of a thin Inconel shield and ceramic inner lining about a coil of Nichrome, yielded 1250 watts at 115 volts, and had a maximum operating temperature of 1500^oF. The nitrogen preheater also employed Calrod units.

The lines from the metering section to the calibration condenser and to the inlet of the fluidized condenser were maintained at the required temperature by serpentine heaters (35). These heaters consisted of a tightly coiled wire spring surrounding small protective Alundum beads over a length of heating element.

The entrance to the fluidized condenser was heated by a Calrod unit.

An improved metering device should be substituted for the capillary-tube metering section now in use. An appropriate substitute would be a Flowrator of the rotameter type, whose fabrication would be limited to the high-temperature, corrosion-resistant stabilized alloys. To facilitate the problem of maintaining the unit at the desired temperature, the float should actuate a controller-recorder instrument.

Further instrumentation would be desirable. For example, close control of the sublimator temperature would diminish fluctuations in the tetrachloride

flow, while multipoint temperature recorders would ease the task of recording the large number of temperatures whose magnitudes are important factors in testing the proposed correlation for the conditions of any run.

A pressure-relief valve should be installed in the sublimator. Precautions should be taken to assure that the relief valve remains free of plugging from condensation of tetrachloride. A high-temperature rupture disc might prove of value in this case.

Nichrome heaters were used almost universally in the present apparatus to maintain various parts of the system at the desired temperature levels. However, Nichrome coils are always subject to burning out, even when operated below the recommended power densities. To alleviate this problem, it is suggested that where applicable, direct-resistance heating be substituted for Nichrome.

The pneumatic-lift recycle system operated satisfactorily for a short time, but could not be made to function all of the time during the two fluidization runs. It is suggested that the recycle system be redesigned to permit the use of a commercial eductor or injector for more efficient operation of the pneumatic lift. In addition, that portion of the recycle system immediately below the fluidized condenser should be redesigned. A more efficient, gas-tight motor-driven rotary star valve and a plug-proof cone feeding the lift should be substituted in the present system.

When zirconium is made, small quantities of nitrogen may combine with the metal to form the nitride which can, even in small amounts, so reduce the ductility of the metal as to ruin it for commercial application. For this reason, it might be wise to prevent possible nitrogen contamination of the zirconium tetrachloride by the use of argon for manometer purging and/or dilution of tetrachloride vapor.

C. DESIGN OF APPARATUS

The critical mass velocity necessary for fluidization was calculated for a batch system from the formula developed by Miller and Logwinuk (26):

$$\text{Critical Mass Velocity} = \frac{0.00125(D_p)^2(\rho_s - \rho)^{0.9}(\rho)^{0.1}(g)}{\mu}$$

Here (g) is the acceleration of gravity in ft./(hr.)(hr.), and other symbols are as defined in the Table of Nomenclature. This equation applies to batch fluidization, and a minimum velocity of 0.1 ft./sec. was thus determined.

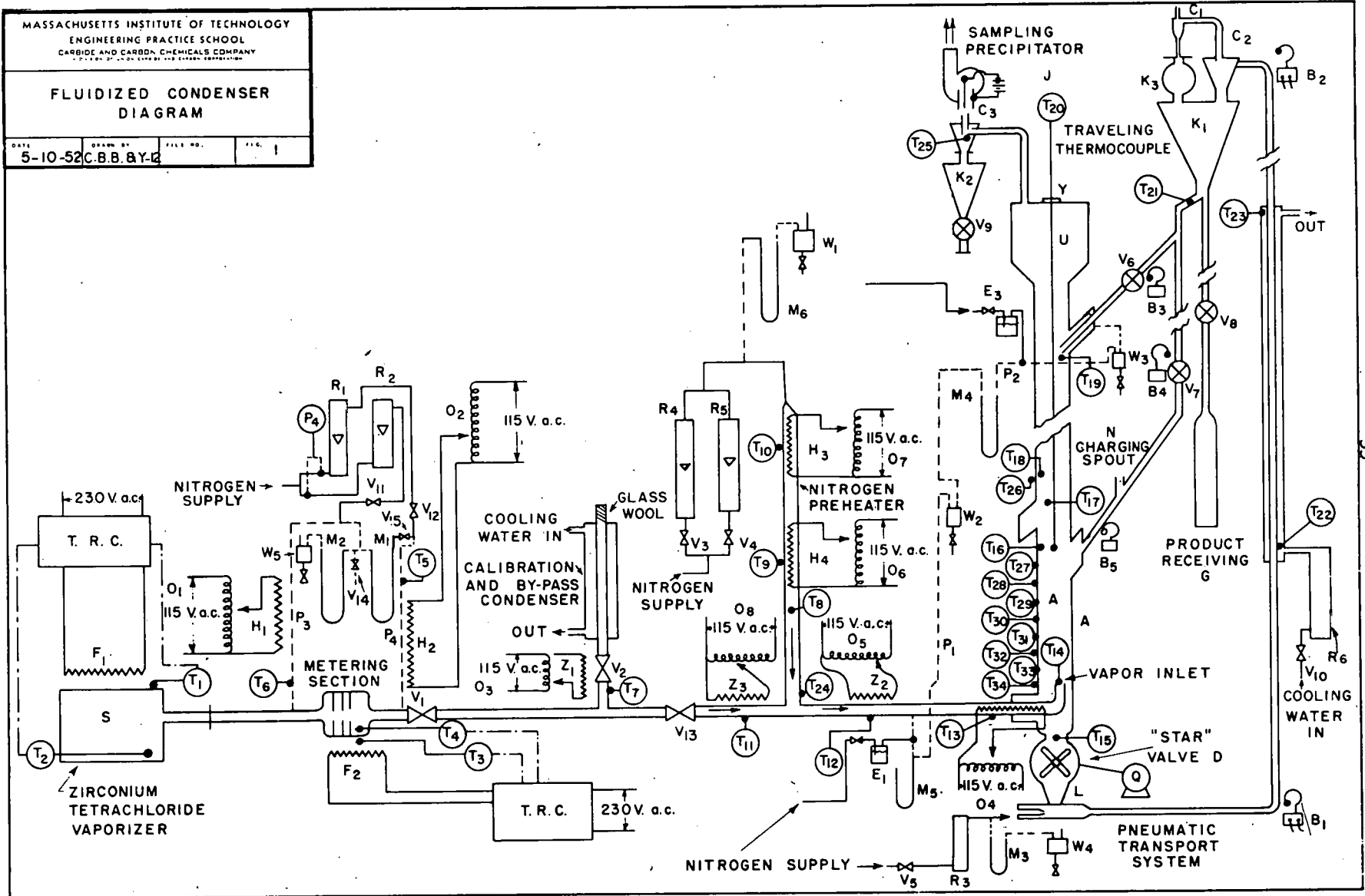
A column of 3 in. I.D. was chosen as a convenient size, and as a compromise between a larger, more expensive column and a smaller column with greater attendant wall effects.

The zirconium tetrachloride flow rate was then determined from the minimum velocity and the desired entrance concentration of $Y_1 = 0.5$. A flow of approximately 40 g./min. was calculated. The next step was the estimation of the pressure drop across the capillary tube of the metering section caused by the vapor flow. Standard formulae (2, 31) were used to determine expansion and contraction friction losses and the friction pressure drop due to the tube itself. The total pressure drop was about 2 in. Hg for a flow of 40 g./min. of zirconium tetrachloride. The dimensions of the capillary tube were 0.125 in. O.D., and 0.075 in. I.D.

The calibration of the Flowrator followed suggested methods (2, 31). Table I lists calibration-run data, the measured pressure drop, and the flow rate.

With the knowledge of the entrance temperatures of the various streams and the desired bed temperature, the recycle rate was determined by a heat balance. Calculation of the recycle rate, approximately 0.5 lb./min. allowed sizing of the auxiliaries of the recycle system. These auxiliaries included conveying system (31), recycle cooler (31, 25), and the cyclone separator (31).

MASSACHUSETTS INSTITUTE OF TECHNOLOGY			
ENGINEERING PRACTICE SCHOOL			
CARBIDE AND CARBON CHEMICALS COMPANY			
FLUIDIZED CONDENSER DIAGRAM			
DATE	DRAWN BY	FILE NO.	FIG. #
5-10-52	C.B.B. & Y.R.		1



LEGEND FOR FIGURE 1

<u>Symbol</u>	<u>Description</u>
A	condenser section.
B-1, B-2	bell ringers, pneumatic-transport system.
B-3, B-4, B-5	bell ringers, solids-recycle lines.
C-1, C-2	cyclone collectors, pneumatic-transport system.
C-3	condenser off-gas fines collector.
D	star rotary valve.
E-1, E-2, E-3	nitrogen bubblers.
F-1, F-2	"Hevi-Duty" clamshell-type furnaces.
G	4000-ml., graduated-cylinder, product receiver.
H-1, H-2	Calrod heaters, zirconium-tetrachloride manometer lines.
H-3, H-4	internal Calrod heaters, nitrogen preheater.
H-5	internal Calrod heater, vapor inlet.
J	portable sampling precipitator.
K-1	4-liter Erlenmeyer collecting bin.
K-2	750-ml. Erlenmeyer fines-collecting bin.
K-3	collecting bin, pneumatic-transport-system fines.
L	nickel transition cone.
M-1, M-2	differential and static manometers, zirconium-tetrachloride flowmeter.
M-3	static manometer, pneumatic-transport-system nitrogen.
M-4	condenser-pressure-drop manometer.
M-5	static manometer, vapor-inlet line.

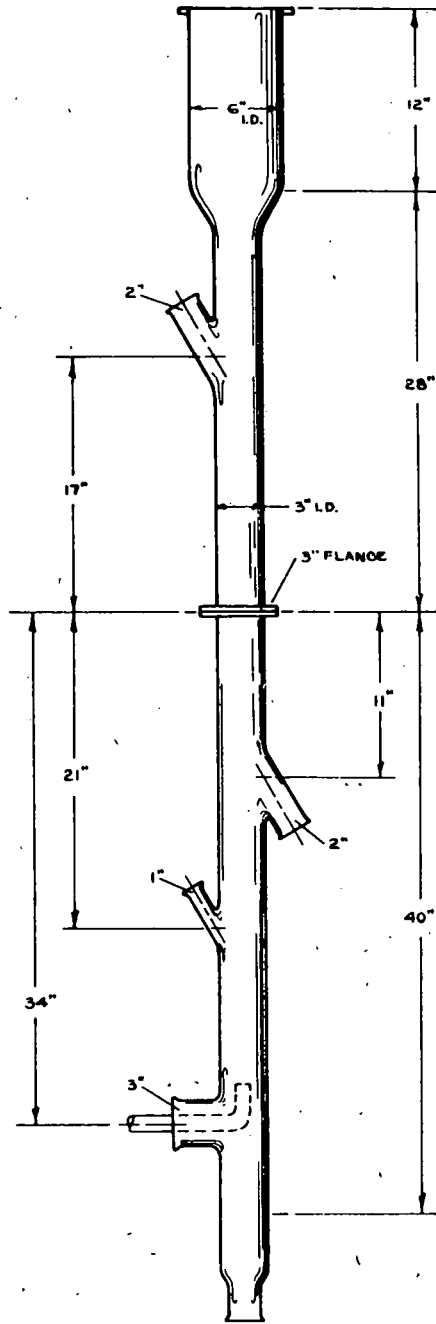
<u>Symbol</u>	<u>Description</u>
M-6	static manometer, preheater nitrogen line.
N	charging spout.
O-1 through O-8	Powerstat transformers.
P-1 through P-4	pressure-transmitting lines.
Q	"Vari-Speed" motor.
R-1, R-2	purge-nitrogen rotameters for zirconium-tetrachloride flowmeter.
R-3	pneumatic-transport-nitrogen rotameter.
R-4, R-5	preheated-nitrogen rotameters.
R-6	cooling-water rotameter for pneumatic-transport system.
S	zirconium-tetrachloride vaporizer.
T	temperature measuring locations.
T-1	vaporizer skin temperature.
T-2	vaporizer bed temperature.
T-3	skin temperatures, zirconium-tetrachloride flowmeter.
T-4	gas temperature, zirconium-tetrachloride flowmeter.
T-5, T-6	skin temperatures, zirconium-tetrachloride-flowmeter pressure lines.
T-7	inlet-line skin temperature, bypass condenser.
T-8	preheated nitrogen temperature.
T-9, T-10	nitrogen preheater skin temperature.
T-11, T-12, T-13	vapor-line skin temperatures.
T-14	mixed-gases temperature.
T-15	solids temperature.

<u>Symbol</u>	<u>Description</u>
T-16	inside wall temperature, 12-1/2 in.
T-17	middle of condenser, 22-1/8 in. from vapor inlet.
T-18	inside wall temperature, 28-3/8 in. from vapor inlet.
T-19	1 in. from wall, upper recycle inlet.
T-20	8-ft. traveling thermocouple, center of condenser.
T-21	cooled recycled-solids temperature.
T-22, T-23	inlet and outlet cooling-water temperatures.
T-24	skin temperature, nitrogen preheater outlet.
T-25	condenser off-gas temperature.
T-26	condenser outside-wall temp., 28-3/8 in. from vapor inlet.
T-27	" " " 10 " " " "
T-28	" " " 8 " " " "
T-29	" " " 7 " " " "
T-30	" " " 6 " " " "
T-31	" " " 5 " " " "
T-32	" " " 4 " " " "
T-33	" " " 2 " " " "
T-34	" " " 1 " " " "
U	expanded section of condenser.
V-1	Monel control valve for zirconium-tetrachloride vapor.
V-2	stainless-steel bypass valve.
V-3, V-4, V-5	brass plug-type nitrogen-control valves.
V-6, V-7	1-in. std. Pyrex stopcocks for recycle control.
V-8, V-9	1-in. std. Pyrex stopcocks.

<u>Symbol</u>	<u>Description</u>
V-10	1-in. plug-type control valve.
V-11, V-12	stopcocks for controlling purge nitrogen.
V-13	shut-off valve for bypassing.
V-14, V-15	manometer shut-off valves.
W-1 through W-4	manometer-fluid traps.
Y	packing gland for T-20.
Z-1, Z-2, Z-3	"Serpentine" flexible heating elements.

Other Symbols

T.R.C.	Brown Instrument Company - temperature recorder-controller.
--------	---



SCALE:
 $\frac{1}{8}'' = 1''$

MASSACHUSETTS INSTITUTE OF TECHNOLOGY ENGINEERING PRACTICE SCHOOL CARBIDE AND CARBON CHEMICALS COMPANY <small>A DIVISION OF CARBIDE AND CARBON, 112 LEXINGTON AVENUE, NEW YORK 17, N.Y.</small>			
CONDENSER COLUMN			
DATE 5-10-52	DRAWN BY CBB	FILE NO.	FIG. 2

D. THEORETICAL ANALYSIS

The theoretical development which follows is based on several assumptions:

1. The vapor pressure of the condensate at the temperature of the bed is negligible;
2. The resistance to heat transfer through the solid particle is negligible compared to the gas-film resistance;
3. The solids in the bed are well mixed and act as a constant-temperature sink at a temperature T_b ;
4. The gas flows upward through the bed in "piston-type" flow with negligible back-mixing;
5. The area for heat transfer is the same as the area for mass transfer;
6. There is no heat loss through the walls of the condenser;
7. The condensable vapor approximates a perfect gas in following the perfect-gas relationship; and
8. The fluidized condenser is operating under steady-state conditions.

1. Properties of the Bed

The properties of the bed at any point may be determined as functions of fundamental quantities.

The total surface area of all the particles in the bed is (A_b).

$$A_b = \frac{(m_b)(L)(S_p)}{(m_p)} = (\phi_b)(L)(S_p) \quad (1)$$

The mass of the bed per unit height is (m_b), the mass per particle is (m_p), the average surface area per particle is (S_p), and the number of solid particles per unit height of bed is (ϕ_b).

If the bed is uniformly distributed over the height,

$$dA_b = (\phi_b)(S_p)(dL). \quad (2)$$

And if (S_b) is the particle surface area per unit height of bed,

$$S_b = (\phi_b)(S_p). \quad (3)$$

Then

$$dA_b = (S_b)(dL) \quad (4)$$

The volume and mass per particle are (v_p) and (m_p) . The particle diameter is (D_p) , and the particle density is (ρ_s) .

$$v_p = \frac{\pi(D_p)^3}{6} \quad (5)$$

$$m_p = \frac{\pi(D_p)^3(\rho_s)}{6} \quad (6)$$

The cross-sectional area of the column is (A_t) , and the column diameter is (D_t) . The column volume per unit height of bed is (v_t) .

$$A_t = \frac{\pi(D_t)^2}{4}, \quad (7)$$

$$v_t = (A_t)(1), \text{ and} \quad (8)$$

$$m_b = (v_t)(\rho_b) = (A_t)(\rho_b) \quad (9)$$

where (ρ_b) is the apparent bed density.

$$\phi = \frac{(m_b)}{(m_p)} = \frac{6(A_t)}{\pi(D_p)^3(Q)} \quad (10)$$

where (Q) is the ratio of the particle density to the apparent bed density.

$$S_p = \pi(D_p)^2 \quad (11)$$

$$S_b = (\phi_b)(S_p) = \frac{6(A_t)(\pi)(D_p)^2}{\pi(D_p)^3(Q)} \quad (12)$$

$$S_b = \frac{6(A_t)}{(D_p)(Q)} \quad (12a)$$

The effective area of heat transfer or mass transfer per unit bed volume is (a).

$$a = \frac{(S_b)}{(v_t)} = \frac{6(A_t)}{(D_p)(Q)(A_t)} = \frac{6}{(D_p)(Q)} \quad (13)$$

The volume of solids per unit height of bed is (v_b).

$$v_b = \frac{(m_b)}{(\rho_s)} = \frac{(A_t)(\rho_b)}{(\rho_s)} = \frac{(A_t)}{(Q)} \quad (14)$$

Then (e), the void fraction of the bed may be described:

$$(1 - e) = \frac{(v_b)}{(v_t)} = \frac{(A_t)}{(Q)(A_t)} = \frac{1}{(Q)} \quad (15)$$

2. Heat and Mass Transfer in Fluid-Solid Systems

If (θ) is an additive property of two constituents of a mixture,

$$\theta = \frac{(\theta_z)(Y) + (\theta_v)}{(1 + Y)} \quad (16)$$

For example, the average molecular weight (M) of the gas mixture may be expressed as a function of the concentration (Y), the molecular weight (M_z) of the condensable gas, and the molecular weight (M_v) of the inert gas.

$$M = \frac{(M_z)(Y) + (M_v)}{(1 + Y)} \quad (17)$$

The superficial mass velocity of the gas mixture is (G).

$$G = \frac{(V)(M)(1 + Y)}{(A_t)} \quad (18)$$

In the above equation, (V) is the molar feed rate of the inert gas.

Garrison (12) represents (j_d), the j-factor, for fixed and fluidized beds as a function of the modified Reynolds number, $6(G)/(a)(\mu)$,

$$j_d = \left(\frac{1}{6^F}\right) \left[\frac{6(G)}{(a)(\mu)}\right]^{-F} (1 - e)^g \quad (19)$$

where (F) is a dimensionless constant, and (μ) is the viscosity of the gas mixture. The exponents (f) and (g) are empirical quantities.

Equation (19) may be combined with equations (13), (15), and (18) so that

$$j_d = \left(\frac{1}{6^F}\right) \left[\frac{6(V)(M)(1 + Y)(D_p)(Q)}{6(A_t)(\mu)}\right]^{-F} \left[\frac{1}{(Q)}\right]^g \quad (20)$$

or

$$j_d = \left(\frac{1}{6^F}\right) \left[\frac{(D_p)(V)(M)(1 + Y)}{(A_t)(\mu)}\right]^{-F} \left[\frac{1}{(Q)}\right]^{g+F} \quad (20a)$$

The Reynolds number used in this work is defined as

$$N_{Re} = \frac{(D_p)(V)(M)(1 + Y)}{(A_t)(\mu)} \quad (21)$$

Then

$$j_d = \left(\frac{1}{6^F}\right) (N_{Re})^{-F} (Q)^{-(g+F)} \quad (22)$$

The following quotation is from Benedict and Thompson (4):

"The principles of heat and mass transfer which are used in this study have been extensively developed. Colburn (7) presented a theoretical relationship between mass transfer and friction drop based on the Reynolds analogy, which was substantiated by data for fluids inside tubes. He continued this work (8), introducing

j-factor plots to correlate heat-transfer and friction data for various types of surfaces. Finally Chilton and Colburn (6) pointed out that the Reynolds analogy as applied to heat and mass transfer should be valid for most types of surfaces, since the mechanisms are so closely similar.

"These relationships between heat and mass transfer have been used to design equipment in which both processes occur simultaneously. The design of condensers from the point of view of heat-transfer surface required is described by Colburn and Hougen (9). The phenomenon of mist formation from a saturated mixture is treated by Colburn and Edison (10), and essentially the same approach will be used in the present study.

"Chilton and Colburn (6) presented the following relationship between heat and mass transfer rates based on the Reynolds analogy. The dimensionless factor, j, is found in the case of turbulent flow to be a function of the Reynolds number with mass velocity and diameter suitably defined for each type of surface."

$$j = \frac{(K)(p_m)(M)}{G} \left[\frac{(\mu)}{(\rho)(D_v)} \right]^m = \frac{(K)(p_m)(M)(N_{Sc})^m}{G} \quad (23)$$

$$j = \frac{h}{CG} \left(\frac{C\mu}{k} \right)^m = \frac{h(N_{Pr})^m}{CG} \quad (23a)$$

In these equations, (K) is the mass-transfer coefficient, (p_m) is the logarithmic-mean film partial pressure of the inert gas, (D_v) is the diffusivity of the gas mixture, (N_{Sc}) is the Schmidt number of the gas mixture, (h) is the convective heat-transfer coefficient, (C) is the specific heat at constant pressure of the gas mixture, (k) is the thermal conductivity of the gas mixture, (N_{Pr}) is the Prandtl number of the gas mixture, and (m) is an empirical exponent. The density of the gas mixture is (ρ).

Eliminating (j) from equations (23a) and (22),

$$\frac{h(N_{Pr})^m}{CG} = \frac{(N_{Re})^{-f} (Q)^{-(g+f)}}{6F} \quad (24)$$

$$h = \frac{(C) (V) (M) (1 + Y) (N_{Pr})^{-m} (N_{Re})^{-f} (Q)^{-(g+f)}}{6(A_t) (F)} \quad (25)$$

Again quoting from Benedict (4),

"The principles of heat and mass transfer described above will now be used to develop relationships which can be used in the design of condensation equipment. The subject divides naturally into two parts: (1) superheated gas mixtures in which condensation takes place only at a cold surface, and (2) saturated gas mixtures in which condensation takes place both at the cold surface and in the main body of the gas."

3. Superheated Gas Mixtures

The rate of condensation from a superheated gas mixture is given by the rate equation

$$\frac{-V(dY)}{dA_b} = (K) (p_{z1} - p_{zb}) \quad (26)$$

From equation (23),

$$K = \frac{(G) (h) (N_{Pr})^m (N_{Sc})^{-m}}{(M) (C) (G) (p_m)} = \frac{(h) (N_{Le})^m}{(C) (M) (p_m)} \quad (27)$$

Here (p_{z1}) is the partial pressure of the condensable gas on the gas-stream side of the gas film surrounding a particle in the bed, (p_{zb}) is the partial pressure of the condensable gas on the solid side of the gas film surrounding each particle in the bed, and (N_{Le}) is the Lewis number of the gas mixture, i.e., the ratio of the Prandtl number to the Schmidt number.

Combining equations (26) and (27),

$$\frac{-V (dY)}{dA_b} = \left(\frac{h}{CM} \right) (N_{Le})^m \left(\frac{p_{z1} - p_{zb}}{p_m} \right) \quad (28)$$

But

$$p_m = \frac{(p_{vb} - p_{v1})}{\ln \left(\frac{p_{vb}}{p_{v1}} \right)} = \frac{(P - p_{zb}) - (P - p_{z1})}{\ln \left(\frac{P - p_{zb}}{P - p_{z1}} \right)} \quad (29)$$

$$P_m = \frac{(p_{z1} - p_{zb})}{\ln \left(\frac{P - p_{zb}}{P - p_{z1}} \right)} \quad (29a)$$

The vapor pressure of the solid at the temperature of the bed will be low so that (p_{zb}) is approximately 0. In the above equations, (p_{vb}) is the partial pressure of the inert gas on the solid side of the gas film surrounding each particle in the bed, (p_{v1}) is the partial pressure of the inert gas on the gas-stream side of the gas film surrounding each particle in the bed, and (P) is the total pressure in the bed.

$$\frac{(p_{z1} - p_{zb})}{(P_m)} = \left(\frac{p_{z1} - p_{zb}}{P - p_{zb}} \right) \ln \left(\frac{P - p_{zb}}{P - p_{z1}} \right) = \ln \left(\frac{P}{P - p_{z1}} \right) \quad (30)$$

But (Y) has been defined so that

$$p_{z1} = \frac{YP}{(1 + Y)} \quad (31)$$

$$\frac{(p_{z1} - p_{zb})}{(P_m)} = \ln \left(\frac{P}{P - p_{z1}} \right) = \ln \left(\frac{P}{P - \frac{YP}{(1+Y)}} \right) = \ln(1 + Y) \quad (32)$$

Combining equations (28) and (32),

$$\frac{-V (dY)}{dA_b} = \frac{h (N_{Le})^m \ln(1 + Y)}{CM} \quad (33)$$

Or

$$\frac{(h) (dA_b)}{(V)} = \frac{(M) (C) (dY)}{(N_{Le})^m \ln(1 + Y)} \quad (34)$$

Quoting from Benedict (4),

"The temperature gradient from the point where the gas mixture enters the column to the point where saturation is reached is determined by equating the loss in sensible heat of the gas to the heat carried to the solids by convection."

$$-(V) (1 + Y) (M) (C) (dT) = (h) (T - T_b) (dA_b) \quad (35)$$

Or

$$\frac{(h) (dA_b)}{(V)} = \frac{(1 + Y) (M) (C) (dT)}{(T - T_b)} \quad (36)$$

In these equations, (T) is the temperature of the gas mixture, and (T_b) is the bed temperature.

Equations (34) and (36) may now be combined.

$$\frac{(M) (C) (dY)}{(N_{Le})^m \ln(1 + Y)} = \frac{(1 + Y) (M) (C) (dT)}{(T - T_b)} \quad (37)$$

Or

$$\int_{T_1}^{T_s} \frac{dT}{(T - T_b)} = \int_{Y_1}^{Y_s} \frac{dY}{(N_{Le})^m (1 + Y) \ln(1 + Y)} \quad (38)$$

$$\ln \left(\frac{T_s - T_b}{T_1 - T_b} \right) = \int_{Y_1}^{Y_s} \frac{dY}{(N_{Le})^m (1 + Y) \ln(1 + Y)} \quad (39)$$

Here, (T₁) is the entrance temperature of the gas mixture, and (T_s) is the temperature of the gas mixture when saturation is first reached. Equation (39) may be integrated graphically, or, if (N_{Le}) is constant over the range (T_s) < (T) < (T₁) and (Y_s) < (Y) < (Y₁), then

$$\ln \left(\frac{T_s - T_b}{T_1 - T_b} \right) = (N_{Le})^m \ln \left(\frac{\ln(1 + Y_s)}{\ln(1 + Y_1)} \right) \quad (40)$$

The equation relating the vapor pressure to the saturation temperature is available from the literature (30).

$$\log_{10} P_z = f(T) \quad (41)$$

where $f(T)$ denotes some function of temperature.

Combining equations (41) and (31),

$$\log_{10} \frac{YP}{(1+Y)} = f(T). \quad (42)$$

From equation (42), the saturation curve of (Y) vs. (T) may be plotted, and, using equations (39) or (40), the "unsaturation" curve of (T) vs. (Y) , for a given (T_1) and (Y_1) , may be plotted. The point of intersection of these equations is (T_s, Y_s) , the conditions which exist in the bed where saturation is first reached.

The height of bed necessary to reach saturation will now be determined.

Combining equations (4), (12), (25), (33),

$$\frac{-(V)(dY)(C)(M)}{\ln(1+Y)} = \frac{(C)(V)(M)(1+Y)(N_{Pr})^{-m}(N_{Re})^{-f}(Q)^{-(g+f)}(dL)}{(F)(D_p)(Q)(N_{Le})^{-m}} \quad (43)$$

Or

$$\int_0^{L_s} (dL) = - \int_{Y_1}^{Y_s} (F)(D_p)(Q)^n (N_{Re})^f (N_{Sc})^m \left[\frac{dY}{(1+Y) \ln(1+Y)} \right] \quad (44)$$

that is,

$$L_s = - \int_{Y_1}^{Y_s} (F)(D_p)(Q)^n (N_{Re})^f (N_{Sc})^m \left[\frac{dY}{(1+Y) \ln(1+Y)} \right]. \quad (45)$$

Here (L_s) is the height of bed necessary to reach the saturation temperature (T_s) and the saturation concentration (Y_s) . The Reynolds group and the Schmidt group are functions of both temperature and concentration, but no difficulty is encountered in

evaluating them inasmuch as the relationship between (T) and (Y) is already known from equation (40).

Equation (45) may now be integrated graphically, and the height of bed necessary to reach saturation thus determined.

4. Saturated Gas Mixtures

"The method of calculation for a saturated gas is somewhat more involved, since condensation takes place both at the cold surface and in the main body of the mixture.

"If the gas mixture is saturated, it is first necessary to establish whether or not it will remain saturated. This is done by computing the fraction of the condensate which comes out as mist. If the fraction is positive, the gas mixture will tend to remain saturated." (4).

The fraction of condensate appearing as mist is given by (α), where (\int_1) is the rate of diffusion of the condensable gas across the gas film per unit solids area, and (\int) is the total rate of condensation per unit solids area.

$$\alpha = 1 - \frac{\int_1}{\int} \quad (46)$$

As in equation (26)

$$\int (1 - \alpha) = \int_1 = K(p_z - p_{z_b}) = \frac{(h)(N_{Le})^m (p_z - p_{z_b})}{(M)(C)(p_m)} \quad (47)$$

But, as in equation (32),

$$\frac{(p_z - p_{z_b})}{p_m} = \ln(1 + Y) \quad (48)$$

So

$$\int (1 - \alpha) = \frac{(h)(N_{Le})^m \ln(1 + Y)}{(M)(C)} \quad (49)$$

By definition,

$$\int = \frac{-V (dY)}{dA_b} = \frac{-(V) (dY) (dT)}{(dT) (dA_b)} \quad (50)$$

Evaluation of the term $\frac{(dY)}{(dT)}$ may be accomplished by the use of a modified Clausius-Clapeyron equation.

$$\frac{dp}{p} = \frac{\lambda dT}{(R)(T)^2} \quad (51)$$

By equation (31),

$$dp = \frac{(dY)}{(1+Y)} - \left[\frac{(Y)(dY)}{(1+Y)^2} \right] = \frac{(dY)}{(1+Y)^2} \quad (52)$$

so

$$\frac{dp}{p} = \frac{(1+Y)(dY)}{(1+Y)^2(Y)} = \frac{(dY)}{(Y)(1+Y)} \quad (53)$$

Therefore

$$\frac{(dY)}{(Y)(1+Y)} = \frac{\lambda (dT)}{(R) (T)^2}, \quad (54)$$

or

$$\frac{(dY)}{(dT)} = \frac{\lambda(Y)(1+Y)}{(R)(T)^2} \quad (54a)$$

"The temperature gradient, $\frac{(dT)}{(dA_b)}$, is evaluated by equating the loss in sensible heat of the gas, plus the heat of condensation of the material condensing as mist, to the heat transferred to the solid by convection." (4)

$$(h)(dA_b)(T - T_b) = (\lambda)(\int - \int_1)(dA_b) - (V)(1+Y)(M)(C)(dT) \quad (55)$$

From equation (46),

$$\alpha = \frac{\int - \int_1}{\int} \quad (56)$$

$$\int \alpha = \int - \int 1 \tag{57}$$

or equation (55) becomes

$$(h) (T - T_b) = (\lambda)(\int)(\alpha) - [(V)(1 + Y)(M)(C)] \left(\frac{dT}{dA_b} \right) \tag{58}$$

Combining equations (50) and (54),

$$\int = \frac{-(V)(Y)(1 + Y)(\lambda)(dT)}{(R)(T)^2 (dA_b)} \tag{59}$$

In the above equations, (R) is the gas constant, (λ) is the latent heat of condensation of the condensable vapor.

Define the terms (a_1) and (a_2) so that

$$a_1 \equiv \frac{(\lambda) (N_{Le})^m \ln(1 + Y)}{(M)(C)} \tag{60}$$

$$a_2 \equiv \frac{(R)(T)^2 (N_{Le})^m \ln(1 + Y)}{(\lambda) (Y)} \tag{61}$$

Then

$$\frac{a_2}{a_1} = \frac{(R)(T)^2(M)(C)}{(Y) (\lambda)^2} \tag{62}$$

From equations (49), (60),

$$\int = (1 - \alpha) \left(\frac{h a_1}{(\lambda)} \right) \tag{63}$$

$$h = \frac{(\lambda)(\int)(1 - \alpha)}{a_1} \tag{63a}$$

From equations (63), (58),

$$\frac{(\lambda)(f)(1 - \alpha)(T - T_b)}{a_1} = \frac{(\lambda)(f)(\alpha)}{a_1} - \left[\frac{(V)(1+Y)(M)(C)}{a_1} \right] \left(\frac{dT}{dA_b} \right) \quad (64)$$

$$\frac{(1 - \alpha)(T - T_b)}{a_1} = \alpha - \left[\frac{(V)(1+Y)(M)(C)}{(\lambda)(f)} \right] \left(\frac{dT}{dA_b} \right) \quad (65)$$

From equation (59)

$$\frac{(1 - \alpha)(T - T_b)}{a_1} = \alpha + \frac{(V)(1+Y)(M)(C)(dT)(R)(T)^2}{(\lambda)(V)(Y)(1+Y)(dA_b)(\lambda)} \left(\frac{dA_b}{dT} \right) \quad (66)$$

This is,

$$\frac{(T - T_b)(1 - \alpha)}{a_1} = \alpha + \left[\frac{(M)(C)(R)(T)^2}{(\lambda)^2 (Y)} \right] \quad (67)$$

From equations (62) and (67),

$$\frac{(T - T_b)(1 - \alpha)}{a_1} = \alpha + \frac{a_2}{a_1} \quad (68)$$

Using equation (68), it may be shown that

$$\alpha = 1 - \left(\frac{a_1 + a_2}{T - T_b + a_1} \right) \quad (69)$$

Returning to equation (58),

$$(h)(T - T_b) = (\lambda)(f)(\alpha) - \left[(V)(1+Y)(M)(C) \right] \left(\frac{dT}{dA_b} \right) \quad (70)$$

or

$$-\left(\frac{dT}{dA_b}\right) = \frac{(h)(T - T_b) - [(\lambda)(\int)(\alpha)]}{(v)(1 + Y)(M)(C)} \quad (71)$$

From equations (63) and (71)

$$-\left(\frac{dT}{dA_b}\right) = \frac{(h)(T - T_b) - \left[\frac{(\lambda)(h)(a_1)(\alpha)}{(\lambda)(1 - \alpha)}\right]}{(v)(1 + Y)(M)(C)} \quad (72)$$

or

$$-\frac{(dT)}{(dA_b)} = \frac{(h)}{(v)(M)(C)(1+Y)} \left[T - T_b - \frac{(a_1)(\alpha)}{(1 - \alpha)} \right] \quad (72a)$$

By the use of equation (69), the above may be reduced to

$$-\frac{(dT)}{(dA_b)} = \frac{(h)(T - T_b + a_1)}{(v)(M)(C)(1+Y) \left[1 + \left(\frac{a_1}{a_2} \right) \right]} \quad (73)$$

or

$$-\frac{(h)(dA_b)}{(v)} = \frac{(1+Y)(M)(C) \left[1 + \left(\frac{a_1}{a_2} \right) \right] (dT)}{(T - T_b + a_1)} \quad (74)$$

Combining equations (4), (12), (25), (74), it may be shown that

$$(dL) = - (F)(D_p)(Q)^n (N_{Re})^f (N_{Pr})^m \frac{\left[1 + \left(\frac{a_1}{a_2} \right) \right]}{(T - T_b + a_1)} (dT) \quad (75)$$

or

$$\int_{L_s}^{L_2} (dL) = - \int_{T_s}^{T_2} (F)(D_p)(Q)^n (N_{Re})^f (N_{Pr})^m \frac{\left[1 + \frac{a_1}{a_2} \right]}{(T - T_b + a_1)} (dT) \quad (76)$$

The left-hand side of this equation, $(L_2 - L_s)$, is the height of bed required to diminish the concentration of the saturated gas

stream from (Y_s) to the desired exit concentration (Y_2), which corresponds to the exit temperature (T_2).

5. Recycle Rate

An overall heat balance may now be written.

$$(C_r)(r)(T_b - T_r) = (V)(\lambda)(Y_1 - Y_2) + [(V)(1+Y_1)(T_1 - T_2)(C)(M)] \quad (77)$$

In this equation, (C_r) is the specific heat of the solid recycle, (r) is the recycle rate, and (T_r) is the temperature of the cooled recycled solids entering the bed. From this equation, the value of (r), the recycle rate of the cooled solids, may be determined.

From the value of (G), as determined in equation (18), the superficial gas velocity (U) may be computed. Then, knowing (D_p), (U), and (ρ_g), the value of (ρ_b) may be determined from the work of Lewis, Gilliland, and Bauer (23).

6. Overall Coefficients

The overall heat-transfer coefficient may be computed.

$$h_o = \frac{(C_r)(r)(T_b - T_r)}{(S_b)(L_2) \left[\frac{(T_1 - T_b) - (T_2 - T_b)}{\ln \left(\frac{T_1 - T_b}{T_2 - T_b} \right)} \right]} \quad (78)$$

or

$$h_o = \frac{(C_r)(r)(T_b - T_r)}{(S_b)(L_2)(T_1 - T_2)} \ln \left(\frac{T_1 - T_b}{T_2 - T_b} \right) \quad (79)$$

Likewise, the overall mass-transfer coefficient may be determined.

$$K_o = \frac{(V)(Y_1 - Y_2)}{(S_b)(L_2) \left[\frac{(P_1 - P_{zb}) - (P_2 - P_{zb})}{\ln \left(\frac{P_1 - P_{zb}}{P_2 - P_{zb}} \right)} \right]} \quad (80)$$

By the use of equation (31), the above equation may be reduced to a more manageable form:

$$K_o = \frac{(V)(1 + Y_1)(1 + Y_2)}{(S_b)(L_2)(P)} \ln \left[\frac{(Y_1)(1 + Y_2)}{(Y_2)(1 + Y_1)} \right] \quad (81)$$

7. Literature Values For Exponents And Coefficient

Preliminary values for the empirical quantities involved in the theoretical analysis may be found in the literature.

(F)	=	0.114	Gamson, (<u>12</u>).
(f)	=	0.41	Ibid.
(g)	=	0.20	Ibid.
(n)	=	1+g+f = 1.61	Ibid.
(m)	=	2/3	Chilton and Colburn (<u>6</u>).

The vapor pressure equation (20) for zirconium tetrachloride, (equation (41)), is:

$$\log_{10} p_z = -\frac{5390}{T} + 11.741.$$

E. SAMPLE CONDENSER DESIGN

A fluidized condenser will be designed to illustrate the use of the theoretical analysis. The literature values for the coefficient and exponents will be employed.

A sample problem might be worded as follows:

It is desired to condense in a 3-in. diameter fluidized condenser one mole (233 lb.) of vaporized zirconium tetrachloride per hour; the vapor enters the column in an inert nitrogen stream in such a concentration that $Y_1 = 0.50$. The entering gas will be at 450°C , the bed temperature must rise no higher than 120°C , and the recycled solids enter the bed at 20°C . Preliminary work for this product shows that the mean particle diameter for this calculation may be about 100 microns.

It is further desired that the concentration of the exit gas be sufficiently low that the degree of condensation will be 99.98%; i.e., one pound of zirconium tetrachloride will be lost for every 5000 lb. entering the column as vapor.

Determine the height of bed in the 3-in. column necessary to give the desired condensation, and also find the recycle rate and the overall transfer coefficients.

Given:

$$\begin{array}{ll} Y_1 & = 0.50 \\ T_b & = 120^\circ\text{C} \\ T_1 & = 450^\circ\text{C} \end{array} \qquad \begin{array}{ll} Y_2 & = 0.0001 \\ T_r & = 20^\circ\text{C} \end{array}$$

A knowledge of the properties of zirconium tetrachloride, nitrogen, and of a mixture of the two will be assumed. Then, given $Y_1 = 0.50$, and moles/hr. of condensable feed = 1.0,

$$V = 1.0/0.50 = 2 \text{ moles/hr. nitrogen feed.}$$

Also, T_2 , corresponding to Y_2 , equals 126°C if the gas is saturated as it leaves the column. By equation (77),

$$(C_r)(r)(T_b - T_r) = (V)(\lambda)(Y_1 - Y_2) + [(V)(1+Y_1)(T_1 - T_2)(C)(M)]$$

and by substitution of the proper values, $(r) = 2800$ lb. of recycle per hour needed to condense 233 lb. of zirconium tetrachloride.

The recycle rate is therefore $2800/233 = 12/1$.

The solid feed rate is $\frac{2800}{(A_t)(3600)} = 15.8 \text{ lb./sec.}(sq.ft.)$

The gas velocity, $(U) = \frac{(V)(1+Y_1)(359)(T_1 + 273)}{(3600)(273)(A_t)} = 16.1 \text{ ft./sec.}$

From the literature (23), $\rho_b = 1.5 \text{ lb./cu.ft.}$ at $D_p = 100 \text{ microns.}$

Then $(Q) = \frac{\rho_s}{\rho_b} = \frac{175}{1.5} = 116.71$.

The temperature at which saturation is first reached may now be determined, using equation (40).

$$\ln \left(\frac{T_s - T_b}{T_1 - T_b} \right) = (N_{Le})^{-m} \ln \left[\frac{\ln(1 + Y_s)}{\ln(1 + Y_1)} \right]$$

From the known values for (C) , (ρ) , (D_v) , (k) , the value of $(N_{Le})^m$ is found to be 0.691.

The vapor-pressure equation for zirconium tetrachloride (20) is

$$\log_{10} P_z = \frac{5390}{-T} + 11.741$$

Solving these two equations simultaneously by numerical substitution and graphical intersection,

$$T_s = 296^\circ\text{C} \quad Y_s = 0.30$$

The height of bed necessary to reach saturation may be found by graphical integration of equation (45).

$$L_s = \int_{Y_1}^{Y_s} (F)(D_p)(Q)^n (N_{Re})^f (N_{Sc})^m \left[\frac{dY}{(1+Y)\ln(1+Y)} \right]$$

Substitution of the literature values for the exponents and coefficient yields $L_s = 1.38$ in. for a change of (Y) from 0.50 to 0.30.

The height of bed required to drop from $Y_s = 0.30$ and $T_s = 296^\circ\text{C}$ to $Y_2 = 0.0001$ and $T_2 = 126^\circ\text{C}$ may be found from equation (76). This equation becomes

$$L_2 - L_s = \int_{296}^{126} \frac{-(0.114)(D)(Q)^{1.61} (N_{Re})^{0.41} (N_{Pr})^{2/3}}{\left[\frac{1 + \frac{a_1}{a_2}}{T - T_b + a_1} \right]} (dT)$$

By plotting this equation and determining the area under the curve, $L_2 - L_s$ may be found to be 1.34 ft., or 16 in.

The total height of bed necessary for the required condensation is $L_2 = 1.46$ ft. or 17-1/2 in.

Overall coefficients may now be determined from equations (79) and (81), whence $h_o = 740$ Btu/(hr.)(sq.ft.)($^\circ\text{F}$), and $K_o = 39.4$ lb.-moles/(hr.)(sq.ft.)(atm.).

Thus, 233 lb. of zirconium tetrachloride may be condensed in one hour by a recycle of 2800 lb./hr. for the given column, with a bed height of 17-1/2 in.; the overall heat-transfer coefficient is 740 Btu/(hr.)(sq.ft.)($^\circ\text{F}$), and the overall mass-transfer coefficient is 39.4 lb.-moles/(hr.)(sq.ft.)(atm.).

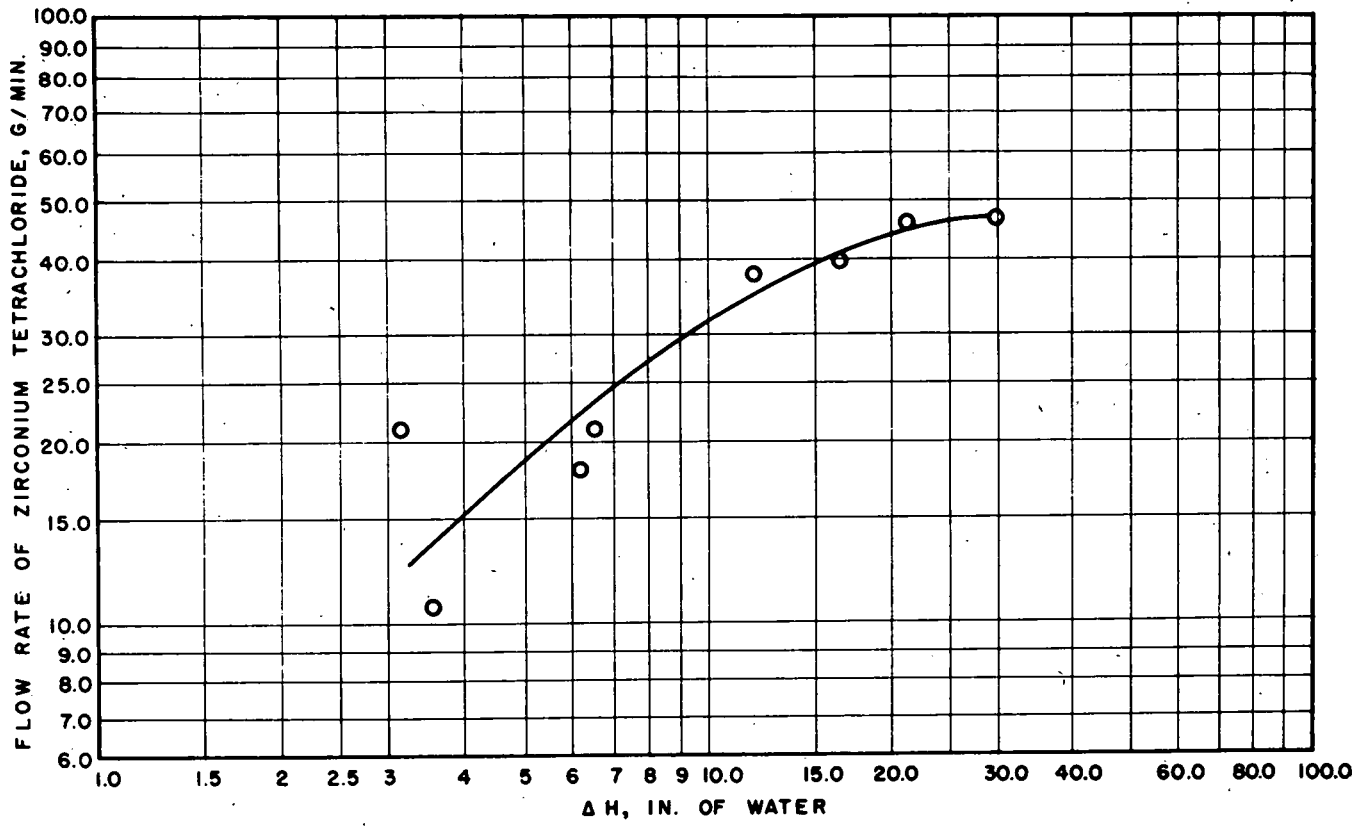
F. EXPERIMENTAL DATA

TABLE I
CALIBRATION OF ZIRCONIUM TETRACHLORIDE FLOWMETER

<u>Date Of Run</u>	<u>Gas Temp.</u> °C	<u>Static Pressure</u> in.Hg	<u>Differential Pressure</u> in. water	<u>Uncorrected Rate of Flow</u> g./min.	<u>Corrected Rate of Flow¹</u> g./min.
Oct.13	427°	2.6	6.2	19.6	17.8
Oct.15	470	0.30	3.07	21.3	20.8
Oct.19	492	1.88	11.8	38.7	37.4
Oct.20	512	2.04	16.4	40.6	39.7
Nov. 1	450	3.0	21.3	49.1	45.3
Nov. 2	450	4.8	6.51	23.3	20.9
Nov. 2	425	1.7	3.54	11.3	10.5
Nov. 3	425	6.45	29.8	53.9	46.4

Note 1: Rate of flow calculated at an upstream pressure of 30 in. mercury absolute and at 500°C.

60



NOTES:

- A. FLOW RATE OF ZIRCONIUM TETRACHLORIDE MEASURED AT 500°C. DOWNSTREAM AND 30 IN. HG. ABS. UP-STREAM PRESSURE.
- B. APPROXIMATELY 2500 CC/MIN. (MEASURED AT 30 IN. HG. AND 70°F) OF PURGE NITROGEN FLOWING INTO EACH MANOMETER TAP.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY ENGINEERING PRACTICE SCHOOL CARBIDE AND CARBON CHEMICALS COMPANY <small>A DIVISION OF CARBIDE AND CARBON CHEMICALS COMPANY</small>			
ZIRCONIUM TETRACHLORIDE FLOW METER CALIBRATION CURVE			
DATE 5-10-62	DRAWN BY GRR	FILE NO.	FIG. 3

TABLE II

PARTICLE SIZE OF BATCH-CONDENSED ZIRCONIUM TETRACHLORIDE

(Not condensed in fluidized operations)

Particle Size (Microns)	<u>Number of Particles</u>				Total No. Particles
	Sample F2-1	Sample F2-9	Sample F3-3	Sample F3-6	
2		2	4	7	13
2	6	2	6	15	29
3	6	5	6	7	24
4.5	12	11	12	13	48
6	13	12	11	9	45
7	24	15	13	13	65
8	11	8	8	6	33
9	10	7	4	4	25
10	3	2	3	3	11
11.5	3	6	2	3	14
13	1	1		2	4
14	2	3		2	7
15		1	1	2	4
16				1	1
				Total	323

Source: T. E. Willmarth, Oak Ridge National Laboratory. (35)

TABLE III

TEMPERATURE RECORD
FLUIDIZATION RUN No. 1

Thermocouple Numbers

	<u>T-7</u>	<u>T-11</u>	<u>T-12</u>	<u>T-13</u>	<u>T-10</u>	<u>T-9</u>	<u>T-24</u>	<u>T-14</u>	<u>T-16</u>
Time, min.	0.2	0.5	1.2	1.3	0.8	0.8	1.7	1.8	2.1
Temp., °C.	420	400	420	420	750	780	210	240	50
Time, min.	6.6	6.8	8.7	8.9	-	10.0	10.3	10.6	10.8
Temp., °C.	415	415	425	415	790	800	230	330	210
Time, min.	15.0	-	15.3	15.4	15.6	-	15.8	16.1	16.3
Temp., °C.	415	425	430	415	790	810	240	350	215
Time, min.	21.9	-	-	-	22.4	-	22.7	-	22.9
Temp., °C.	415	430	430	415	790	810	245	355	210
Time, min.	27.0	-	-	-	-	-	-	-	-
Temp., °C.	410	430	430	415	790	810	250	365	195
Time, min.	33.3	-	-	-	-	-	34.5	-	35.0
Temp., °C.	410	430	430	415	790	810	255	360	155
Time, min.	39.5	-	-	-	-	-	40.6	-	-
Temp., °C.	400	425	430	410	790	805	260	365	135
Time, min.	49.0	-	-	-	-	-	49.9	-	-
Temp., °C.	400	425	425	410	790	805	265	360	115
Time, min.	84.4	-	-	-	-	-	-	-	-
Temp., °C.	400	420	425	405	780	800	265	355	85

TABLE III (Cont'd)

TEMPERATURE RECORD
FLUIDIZATION RUN No. 1

Thermocouple Numbers

	<u>T-17</u>	<u>T-18</u>	<u>T-19</u>	<u>T-5</u>	<u>T-6</u>	<u>T-15</u>	<u>T-21</u>	<u>T-26</u>	<u>T-27</u>
Time, min.	2.5	2.6	2.8	3.2	3.5	3.6	3.8	-	-
Temp., °C.	50	40	40	425	385	40	40	30	30
Time, min.	10.9	11.1	11.3	11.4	11.6	11.7	11.9	-	-
Temp., °C.	150	60	50	420	380	45	40	30	28
Time, min.	16.5	17.1	17.6	18.6	18.7	18.9	19.1	-	-
Temp., °C.	280	140	85	420	380	45	40	70	20
Time, min.	-	23.3	23.5	23.7	-	24.0	-	-	-
Temp., °C.	305	185	120	420	380	45	40	85	20
Time, min.	28.6	-	28.9	-	-	29.3	-	29.7	-
Temp., °C.	305	200	150	420	380	40	40	100	25
Time, min.	-	35.5	-	-	-	-	-	36.3	-
Temp., °C.	300	230	185	420	380	40	40	115	25
Time, min.	-	-	41.7	-	-	-	-	43.0	-
Temp., °C.	300	220	220	418	370	35	35	105	25
Time, min.	-	-	50.9	-	-	-	-	52.0	-
Temp., °C.	285	200	215	415	370	35	35	90	25
Time, min.	-	-	-	-	-	-	-	88.0	-
Temp., °C.	240	160	140	410	360	40	35	60	20

TABLE III (Cont'd)

TEMPERATURE RECORD
FLUIDIZATION RUN No. 1

Thermocouple Numbers

	<u>T-28</u>	<u>T-29</u>	<u>T-30</u>	<u>T-31</u>	<u>T-32</u>	<u>T-33</u>	<u>T-34</u>	<u>T-8</u>	<u>T-25</u>
Time, min.	-	-	-	-	-	-	-	5.7	-
Temp., °C.	75	25	75	80	50	55	45	350	15
Time, min.	-	-	-	-	-	-	-	13.2	-
Temp., °C.	130	25	90	90	50	60	45	370	17
Time, min.	-	-	-	-	-	-	-	20.3	-
Temp., °C.	115	25	95	90	80	75	70	380	18
Time, min.	-	-	-	-	-	-	-	25.5	26.5
Temp., °C.	110	25	90	75	75	75	70	385	23
Time, min.	-	-	-	-	-	-	-	30.8	31.7
Temp., °C.	100	25	75	70	65	70	65	385	25
Time, min.	-	-	-	-	-	-	-	37.5	-
Temp., °C.	95	25	65	65	60	70	60	390	25
Time, min.	-	-	-	-	-	-	-	44.2	-
Temp., °C.	90	25	60	60	55	70	60	390	25
Time, min.	-	-	-	-	-	-	-	53.4	-
Temp., °C.	85	20	50	50	50	70	60	392	25
Time, min.	-	-	-	-	-	-	-	91.0	-
Temp., °C.	70	20	40	45	45	70	55	383	23

TABLE IV

THERMOCOUPLE TRAVERSE
FLUIDIZATION RUN No.1

<u>Location</u> ¹	<u>Temperature, °C</u>	
	<u>After 30 min.</u>	<u>After 85 min.</u>
0 in.	254°	239°
1	259°	
2	259°	
3	259°	
4	259°	237°
5	257°	
7	257°	
8	257°	
10	254°	
12.5	245°	231°
22.1	237°	231°
28.4	237°	233°

Note 1: Inches above point of entrance of nitrogen-tetrachloride mixture to column.

66

TABLE V

METERING SECTION AND NITROGEN PREHEATER DATA
FLUIDIZATION RUN No. 1

Time, min.	<u>Metering-section Manometers</u>				
	<u>Differential Pressure</u> in. liquid sp.gr. 2.95	<u>Static Pressure</u> in.Hg.	<u>Static Pressure*</u> in.liquid sp.gr.2.95	<u>Differential Pressure Across Fluidized Condenser,</u> in. liquid sp.gr. 2.95	<u>Static Pressure, Condenser Inlet,</u> in. liquid sp.gr. 2.95
0	4.7	2.5	4.0	2.0	2.0
3	3.8	2.1	3.3	1.6	2.1
8	5.4	7.2	3.8	2.6	2.0
12	4.6	5.4	2.4	1.0	2.0
27	5.4	7.4	4.8	3.3	4.0
31	4.2	7.2	4.7	3.3	3.9
36.2	4.8	4.4	4.7	3.3	3.9
42	4.8	7.2	4.7	3.2	3.8
51	3.6	1.7	4.1	2.5	3.2
56	5.2	3.0	4.4	2.8	3.5
60	4.1	2.2	4.2	2.7	3.3
67	5.2	2.1	3.8	2.3	3.0
75	3.5	2.2	3.8	1.7	2.0
79	4.5	2.7	4.0	2.0	3.4
84	4.1	2.2	4.1	2.1	-
99	2.0	-	4.0	-	-

*Preheat Nitrogen

67.

TABLE VI
 TEMPERATURE RECORD
 FLUIDIZATION RUN No. 2

<u>Time, Minimum</u>	<u>Thermocouple Numbers</u>									
	<u>T-34</u>	<u>T-33</u>	<u>T-32</u>	<u>T-31</u>	<u>T-14</u>	<u>T-15</u>	<u>T-16</u>	<u>T-17</u>	<u>T-18</u>	<u>T-8</u>
0	25°	25°	25°	25°	375°	35°	120°	105°	40°	-
5	25	25	25	25	383	30	100	140	55	-
11	30	35	35	35	390	30	140	100	70	-
16	35	35	35	35	400	30	120	170	140°	-
22	50	50	50	50	415	35	120	150	135	-
29	50	58	50	50	415	35	160	190	120	-
35	55	55	55	55	420	35	115	130	118	-
43	-	-	-	-	420	35	110	120	105	440°
47	70	70	70	70	350	-	-	-	-	350

TABLE VII
Part I
METERING SECTION AND NITROGEN PREHEATER DATA
FLUIDIZATION RUN No. 2

Time, min.	<u>Metering-section Manometers</u>			<u>Differential Pressure Across Fluidized Condenser, in. liquid sp.gr. 2.95</u>
	<u>Differential Pressure in. liquid sp.gr. 2.95</u>	<u>Static Pressure in.Hg.</u>	<u>Static Pressure Preheat Nitrogen in. liquid sp.gr. 2.95</u>	
0	4.5 in.	10 in.	8.3 in.	1.5 in.
5	4.0	12	5.4	3.5
11	3.8	11.2	4.0	1.8
16	5.0	13.0	5.8	3.4
22	3.8	12.4	6.0	3.6
29	3.0	12.4	5.0	3.4
35	3.5	12.6	7.0	4.3
43	4.0	15.0	8.6	8.6

TABLE VII
Part II

METERING SECTION AND NITROGEN PREHEATER DATA
FLUIDIZATION RUN No. 2

<u>Time, Minimum</u>	<u>Static Pressure, Condenser Inlet, in. liquid sp.gr. 2.95</u>	<u>Bed Height</u> ¹
0	6 in.	23 in.
5	3.5	23
11	2.8	23
16	3.6	23
22	4.1	49
29	3.2	0
35	4.8	40
43	6.3	58

Note 1: Inches above point of entrance of nitrogen-tetrachloride mixture to column.

DISCUSSION OF DATA

1. Fluidization Run No. 1, November 10, 1951, Tables III, IV, V.

At the start of the run, the bed height was about 20 in. above the gas inlet. Because of caking on the walls, it was not possible to determine the bed height during the body of the run. After 84 minutes of operation, it was observed that the top of the bed had risen to the top of the column. At this time, a small amount of cold tetrachloride powder was added to the bed from the recycle holdup bin.

No effect of this addition on the bed height was noticed.

Six minutes after the start of the run, it was attempted to begin recycle by supplying nitrogen to the pneumatic lift. Flow of cooling water to the heat exchanger used to cool the recycle was also begun. The cone feeding the pneumatic lift and the pneumatic lift soon gave evidence of plugging. Although nitrogen flow to the lift was maintained for an hour and repeated attempts to clear the line and cone were made, the plugging persisted. During Run No. 1, there was essentially no recycle of zirconium tetrachloride powder.

A significant consequence of this fact was that all heat transfer had to occur through the walls of the column, so that condensation on the walls was rapid. The decrease in the cross-sectional area of the bed forced the bed up to the top of the column as reported above.

The average flow of zirconium tetrachloride to the condenser, as calculated from the measurement of the pressure drop through the capillary tube of the metering section, was 44.0 g./min. or 0.0772 lb. moles/hr. The average flow of diluent nitrogen through the preheater was 0.0464 lb.-moles/hr., while an equivalent amount, or approximately 0.047 lb.-moles/hr., of nitrogen was passed through the pressure taps of the metering section as a purge to prevent plugging.

The electrostatic precipitator which had been prepared to

sample the exit gas from the column was found to have an electrical defect, and could not be used.

Table IV gives the temperatures indicated by the traveling thermocouple, (T-20). According to Kettenring, Manderfield, and Smith (18), this temperature should correspond to the gas temperature at the particular point in the column. However, the measured values are practically constant, and independent of location. It would seem that the solids in the bed might be influencing this thermocouple, as indicated temperature may be a composite of the gas temperature and the solids temperature.

The run was terminated after 100 minutes of operation.

2. Fluidization Run No. 2, November 11, 1951, Tables VI, VII

For the second fluidization run, recycle was added manually to the top of the column at a rate of approximately 0.5 lb./min. A suitable amount of hot bed material was withdrawn manually from the bottom of the column in an attempt to maintain the bed at a reasonable height. However, the bed height did drop to zero for 3 minutes after 29 minutes of operation (Table VII).

Caking did occur during the second run in the first 12 in. of the column, directly above the gas inlet. The maximum cake thickness was 1/4 in. It is believed that this caking occurred during the short interval when the bed level had dropped below the gas inlet, as mentioned above.

The walls of the remainder of the column showed no caking. The walls of the column at a height greater than 55 in. above the gas inlet were covered by a layer of powder 1/16 to 1/8 in. thick which could be removed by slight tapping on the outside of the column. Had the fluidized bed reached this level, the abrasive action of the fluidized solids would probably have scrubbed the walls clean.

It can be seen that the wall and bed temperatures (Table VI) of this run are considerably lower than the corresponding temperatures of Run No. 1. In each case, the exit concentration of the gas leaving the column could only be estimated, but seemed to be fairly low, i.e., the saturation concentration at a temperature of about 100°C. Again, further temperature data are necessary for any conclusions to be drawn.

The average zirconium-tetrachloride flow rate as determined from the metering section was 0.0741 lb.-moles/hr., while the diluent nitrogen flow through the preheater was 0.0719 lb.-mole/hr. and the purge nitrogen rate was about 0.047 lb.-moles/hr. Thus, the concentration of the condensable tetrachloride was considerably lower for the second run than for the first.

The second run was terminated after 43 minutes of operation.

Table II lists particle sizes of batch-condensed zirconium tetrachloride, as determined by T. E. Willmarth (35). These samples were prepared by passing hot zirconium-tetrachloride vapor into a cold receptacle, and allowing condensation to take place. The identifying numbers "F2-1", "F2-9", etc., refer to operating runs conducted by the personnel of the Y-12 Plant of the Carbide and Carbon Chemicals Company.

Theoretical and experimental work on this thesis was carried out from July 16 to November 17, 1951, at the M.I.T. Practice School, K-25 Plant, and in the Y-12 Area, of the Carbide and Carbon Chemicals Company, a division of Union Carbide and Carbon Corporation, at Oak Ridge, Tennessee. The apparatus described in this report is located in the Y-12 Area, Oak Ridge, Tennessee.

G. NOMENCLATURE

A_b	Total surface area of all the particles in the bed, sq.ft.
A_t	Cross-sectional area of the column, sq.ft.
a	Surface area of the bed per unit column volume, sq.ft./cu.ft.
C	Specific heat, at constant pressure, of the gas stream, Btu/(lb.)($^{\circ}$ F).
C_r	Specific heat of the recycled solids, Btu/(lb.)($^{\circ}$ F).
D_p	Mean diameter of the particles in the bed, ft.
D_t	Diameter of the column, ft.
D_v	Diffusivity of the gas mixture, sq.ft./hr.
e	Void fraction in the bed, dimensionless.
F	Coefficient, Gamson's equation (<u>12</u>); see equation (19).
f	Exponent, Gamson's equation (<u>12</u>); see equation (18).
g	Exponent, Gamson's equation (<u>12</u>); see equation (17).
G	Superficial mass velocity of the gas mixture, lb./(hr.)(sq.ft.)
h	Convective heat-transfer coefficient, Btu/(hr.)(sq.ft.)($^{\circ}$ F).
h_o	Overall heat-transfer coefficient, Btu/(hr.)(sq.ft.)($^{\circ}$ F)
j, j_d, j_h	Mass-or heat-transfer j-factor, dimensionless.

- K Mass-transfer coefficient, lb.-moles/(hr.)(sq.ft.)(atm.).
- K_o Overall mass-transfer coefficient, lb.-moles/(hr.)(sq.ft.)(atm.).
- k Thermal conductivity of the gas mixture, Btu/(hr.)(sq.ft.)($^{\circ}$ F per ft.).
- L Height from the entrance to the bed, ft.
- L_s Height of bed necessary for the gas stream to reach saturation, ft.
- L_2 Total bed height, ft.
- M Molecular weight of the gas mixture, lb./lb.-mole
- m Exponent, Chilton and Colburn relationship (6); see equation (23).
- m_b Mass of bed per unit height of column, lb./ft.
- m_p Average mass of a particle in the bed, lb.
- N_{Le} The Lewis number of the gas mixture, equal to the ratio of the Prandtl number to the Schmidt number, as defined in equation (27), dimensionless.
- N_{Pr} The Prandtl number of the gas mixture, as defined by equation (23a), dimensionless.
- N_{Sc} The Schmidt number of the gas mixture, as defined by equation (23), dimensionless.
- N_{Re} The Reynolds number of the gas mixture, as defined by equation (21), dimensionless.

- n Exponent, equation (44), equal to $(1 + f + g)$, dimensionless.
- P Absolute pressure at a given point in the bed, atm.
- P_m Logarithmic-mean film partial pressure of the inert gas at a given point in the column, atm.
- P_1 Partial pressure of the condensable gas in the gas mixture entering the column, atm.
- P_2 Partial pressure of the condensable gas in the gas mixture leaving the column, atm.
- P_{v1} Partial pressure of the inert gas on the gas-stream side of the gas film surrounding each particle in the bed, atm.
- P_{vb} Partial pressure of the inert gas on the solid side of the gas film surrounding each particle in the bed, atm.
- P_{z1} Partial pressure of the condensable gas on the gas-stream side of the gas film surrounding each particle in the bed, atm.
- P_{zb} Partial pressure of the condensable gas on the solid side of the gas film surrounding each particle in the bed, atm.
- Q Ratio of particle density of the recycled solids to the apparent density of the fluidized bed, $= \rho_s/\rho_b$, dimensionless.
- R The gas constant, $\text{Btu}/(\text{lb.}-\text{mole})(^\circ\text{R})$.
- r Recycle rate of cooled solids, $\text{lb.}/\text{hr}$.
- S_b Average particle surface area per unit height of column, $\text{sq.ft.}/\text{ft}$.
- S_p Average surface area per particle, sq.ft .

- T Temperature of the gas mixture at any given point in the column, $^{\circ}\text{F}$.
- T_1 Temperature of the gas mixture entering the column, $^{\circ}\text{F}$.
- T_2 Temperature of the gas mixture leaving the column, $^{\circ}\text{F}$.
- T_b Temperature of the bed, $^{\circ}\text{F}$.
- T_s Temperature of the gas mixture at the point when saturation is first reached, $^{\circ}\text{F}$.
- T_r Temperature of the cooled recycled solids entering the bed, $^{\circ}\text{F}$.
- U Superficial velocity of the gas mixture at any given point in the column, ft./sec.
- V Feed rate of inert gas to the column, moles/hr.
- v_b Volume of solids per unit height of column, cu.ft./ft.
- v_p Particle volume, cu.ft./particle.
- v_t Column volume per unit height of column, cu.ft./ft.
- Y Moles of condensable gas per mole of inert gas, dimensionless.
- Y_1 Moles of condensable gas per mole of inert gas in the gas mixture entering the column, dimensionless.
- Y_s Moles of condensable gas per mole of inert gas at the point in the column where saturation is first reached, dimensionless.
- Y_2 Moles of condensable gas per mole of inert gas in the gas mixture leaving the column, dimensionless.

α Fraction of the condensate appearing as mist, dimensionless.

\int Total rate of condensation per unit solids area, lb.-moles/(hr.)(sq.ft.).

\int_1 Rate of diffusion of condensable gas across the gas film per unit solid area, lb.-moles/(hr.)(sq.ft.).

θ Any additive property of a gas mixture.

λ Latent heat of condensation of the condensable, Btu/lb.-mole.

μ Viscosity of the gas mixture, lb.-mass/(hr.)(ft.).

ρ Density of the gas mixture, lb./cu.ft.

ρ_b Apparent density of the fluidized phase, lb./cu.ft.

ρ_s Density of the solid particle, lb./cu.ft.

ϕ_b Number of solid particles per unit height of column, (ft.)⁻¹

Subscripts

z Refers to the condensable gas.

v Refers to the inert gas.

H. LITERATURE CITATIONS

- (1) Agarwal, O.P., and Storrow, J.A., Chem. & Ind., 284, 278-286, also 321-324 (1951).
- (2) American Gas Association, "Gas Measurement-Committee Report No. 2," A.G.A., 420 Lexington Avenue, New York (1951).
- (3) Amundson, N.R., and Carr, N.L., Ind. Eng. Chem., 43, 1856-1862 (1951).
- (4) Benedict, M., and Thompson, W.I., Engineering Developments in the Gaseous Diffusion Process, Chap. 6, McGraw-Hill Book Company, New York, (1951).
- (5) Campbell, J.R., and Rumford, F., Soc. Chem. Ind. Jour., 69, 373-377 (1950).
- (6) Chilton, T.H., and Colburn, A.P., Ind. Eng. Chem., 26, 1183 (1934).
- (7) Colburn, A.P., Ind. Eng. Chem., 22, 967 (1930).
- (8) Colburn, A.P., Trans. Am. Inst. Chem. Engrs., 29, 174 (1933).
- (9) Colburn, A.P., and Hougen, O.A., Ind. Eng. Chem., 26, 1178 (1934).
- (10) Colburn, A.P., and Edison, A.G., Ind. Eng. Chem., 33, 457 (1941).
- (11) Ergum, S., and Orning, A.A., Ind. Eng. Chem., 41, 1179 (1949).
- (12) Gamson, B.W., Chem. Eng. Prog., 47, 19-28 (1951).
- (13) Gilliland, E.R., and Mason, E.A., Ind. Eng. Chem., 41, 1148-60 (1949).

- (14) Hariu, D.H., and Molstad, M.C., Ind. Eng. Chem., 41, 1148-60 (1949).
- (15) Hougen, O.A., and Watson, K.M., Chemical Process Principles, John Wiley & Sons., Inc., New York, (1950).
- (16) Kasten, P.R., and Amundson, N.R., Ind. Eng. Chem., 42, 1341-1346 (1950).
- (17) Kelley, K.K., "Contributions to the Data on Theoretical Metallurgy," Bureau of Mines, U.S. Dept. of the Interior (1944).
- (18) Kettenring, K.N., Manderfield, E.L., and Smith, J.N., Chem. Eng. Prog., 46, 139-146 (1950).
- (19) Kiddo, G., Chem. Eng., 56, 112 (1949).
- (20) Kuhn, D.W., Ryan, A.D., and Palko, A.A., Report No. Y-552, Y-12 Plant, C&CCC, (1950).
- (21) Leva, M., et al., Chem. Eng. Prog., 44, 511-20 (1948).
- (22) Leva, M., Weintraub, M., and Grummer, M., Chem. Eng. Prog., 45, 563 (1949).
- (23) Lewis, W.K., Gilliland, E.R., and Bauer, W.C., Ind. Eng. Chem., 41, 1104-1117 (1949).
- (24) Lewis, W.K., Gilliland, E.R., and Sweeney, M.P., Chem. Eng. Prog., 47, 251-256 (1951).
- (25) Mickley, H.S., and Trilling, C.A., Ind. Eng. Chem., 41, 1135-1147 (1949).
- (26) Miller, C.O., and Longwinuk, A.K., Ind. Eng. Chem., 43, 1220-1226 (1951).

- (27) Morse, R.D., and Ballou, C.O., Chem. Eng. Prog., 47, 199-204 (1951).
- (28) Munro, W.D., and Amundson, N.R., Ind. Eng. Chem., 42, 1481-1488 (1950).
- (29) Nicholson, E.W., et al., Ind. Eng. Chem., 40, 2033 (1948).
- (30) Nord, M., Chem. Eng., 58, 157-166 (1951).
- (31) Perry, J.H., ed., Chemical Engineer's Handbook, McGraw-Hill Book Company, Inc., New York (1950).
- (32) Titan Mfg. Co., Advertising Brochure, Buffalo, N.Y. (1951).
- (33) Valentine, S., and Wilhelm, W.H., Ind. Eng. Chem., 43, 1199-1203 (1951).
- (34) Williams, Joe, Private Communication, Y-12 Plant, C&CCC, Oak Ridge (1951).
- (35) Willmarth, T.E., Private Communication, ORNL, C&CCC, Oak Ridge (1951).
- (36) Zenz, F.A., Ind. Eng. Chem., 41, 2801 (1949).

1-80

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

