STATEMENT OF PROBLEM

Letter of Transmittal

STUDENT CHAPTERS - AMERICAN INSTITUTE OF CHEMICAL ENGINEERS
Open Only to Undergraduates or Those Without a Degree in Chemical Engineering

DEADLINE FOR MAILING
Must be postmarked Not Later than Midnight, May 16, 1949

RULES OF THE CONTEST

Solutions will be graded on (a) substantial correctness of results and soundness of conclusions, (b) ingenuity and logic employed, (c) accuracy of computations, and (d) form of presentation. Accuracy of computations is intended to mean primarily freedom from mistakes; extreme precision is not necessary.

It is to be assumed that the statement of the problem contains all the pertinent data except for those readily available in handbooks and similar reference works. The problem is not to be discussed with any person whatever until after May 16, 1949. This is particularly important in cases where neighboring institutions may not begin the problem until after its completion by another chapter. The use of textbooks, handbooks, journal articles, and lecture notes is permitted. In cases where there is disagreement in the data reported in the literature the values given in the statement of the problem have been chosen as being most nearly applicable. Submittal of a solution for the competition implies adherence to the above conditions.

A period of not more than 24 consecutive days is allowed for completion of the solution. This period may be selected at the discretion of the individual counselor, but a solution must be postmarked not later than midnight, May 16, 1949, in order to be eligible. If at all possible the solution should be typewritten and should be accompanied by a letter of transmittal giving only the contestant's name, school address, home address, and student chapter, lightly attached to the report. This letter will be retained for identification by the Secretary of the Institute. The solution itself must bear no reference to the student's name or institution by which it might be identified. In this connection, graph paper bearing the name of the institution should be avoided.

Each counselor should select the best solution, or solutions, from his chapter not to exceed two in number, and send these by registered mail to: Mr. Stephen L. Tyler, Secretary, American Institute of Chemical Engineers.

1949 AIChE STUDENT CONTEST PROBLEM

Prepared by F. Robert Morley, Joseph Koslov, Don Lee Stockton, Reed Burtsfield, and Herbert E. Silcox, Chairman

TO THE CONTESTANT:

During the war DDT was introduced as an insecticide; one of the materials used in its preparation is chloral. Prior to the advent of DDT, chloral was made in small quantities by the chlorination of ethyl alcohol. When the preparation of relatively large quantities of chloral was required for DDT, it became necessary to improve and expand the existing process, particularly from a chemical engineering point of view. A problem encountered during this development has been selected as this year's contest problem.

The chlorination of alcohol to chloral gives rise to an off-gas composed primarily of hydrogen chloride. This off-gas contains unreacted chlorine. The recovery of this chlorine would reduce chloral production costs not only by way of increased chlorine efficiency but also by reducing waste disposal charges. One of the chlorine recovery methods investigated was the use of a recirculating alcohol scrubber. The optimum chlorine recovery and the design of such a recovery unit are the objectives of this year's contest problem.

Certain simplifying assumptions have been made in the presentation of the problem. When these assumptions affect the solution of the problem, the basis for the assumption is included.

THE COMMITTEE

TO JOHN DOE, DESIGN ENGINEER:

The off-gas encountered in the chlorination of alcohol is produced at a rate of 150 cubic feet per minute (70°F. - 3 lb./sq. in gage) and has the following composition (by volume):

Hydrogen chloride	75 per cent
Chlorine	15 per cent
Ethyl chloride	10 per cent

The recovery of chlorine from this off-gas would result in both increased chlorine efficiency and decreased waste disposal charges.

The Chemical Engineering Development Section has been studying possible methods for the recovery of the chlorine in this off-gas. A method has been proposed wherein the off-gas is passed through a scrubbing tower, countercurrent to a recirculating stream of partially chlorinated alcohol (PCA). The chlorine in the off-gas is absorbed and reacts with the partially chlorinated alcohol. The remaining off-gas is passed through a condenser to the existing hydrogen chloride recovery unit. The operation of the unit is to be continuous and the volume and composition of the partially chlorinated alcohol is maintained by continuously withdrawing solution from the system and continuously adding fresh alcohol (Formula 2B) make-up. The solution withdrawn from the recovery system would be used in the existing chlorinators for the preparation of chloral.

The Chemical Engineering Development Section has operated this process on a small scale. Discussion and data pertinent to this process are presented. Based on this information, it is desired to establish the following in terms of the per cent chlorine in the exit gas:

1) The "break-even" point (where the annual operating cost is equal to the gross annual savings).

2) The maximum net annual savings and the range in which it occurs.

3) The maximum return on the capital expenditure and the range in which it occurs.

Based on the optimum point of operation, present a suitable design for the recovery unit which should include a flow sheet and equipment specifications.

DISCUSSION OF DATA

Exit Gas Condenser

It is suggested that this unit be designed on the basis of an article which appeared in the Industrial Edition of Industrial and Engineering Chemistry Vol. 26, 1183 (1934). The condenser is to be operated with brine in the jacket and condensation in the tubes. The condenser is to be designed to give an exit gas at a temperature of 15° C.

The following assumptions should be made to simplify the calculations:

1) The exit gas consists of chlorine, hydrogen chloride, and ethyl chloride, but it is to be considered pure hydrogen chloride for estimation of physical properties of the gas film in the condenser.

2) The liquid in the condenser is to be considered PCA free of hydrogen chloride and chlorine when estimating physical properties.

3) A design velocity of 20 ft./sec. should be assigned to the vapor entering the tubes.

4) The average concentrations of both hydrogen chloride and ethyl chloride are given in Table II of Appendix A. They are to be assumed constant throughout the condenser.

5) The chlorine entering the condenser is assumed to pass through the condenser without reaction or absorption.

6) The entering gas is assumed to be saturated with PCA.

7) The diffusivity can be calculated from an equation in Perry's Handbook (p. 1168).

8) The film coefficients (h) of both the liquid and brine films are to be taken as 100 Btu/(hr.)(sq.ft.)(° F.).

9) The average thermal conductivity of the gas in the condenser is to be taken as 0.008 Btu/(hr.)(sq.ft.)(° F./ft.).

Absorption Tower

Chlorine is more readily removed from the gas stream, the lower the degree of chlorination of the recycled partially chlorinated alcohol. However, the amount of partially chlorinated alcohol produced must be equal to or less than that required by the secondary chlorinators which produce the off-gas for the absorption-reaction system. If this condition is not met, an excess of partially chlorinated alcohol will result. A preliminary study in this respect indicated that a partially chlorinated alcohol characterized by a specific gravity of 1.100 (30°C./30°C.) would be satisfactory.

The removal of chlorine was also studied from the standpoint of temperature of operation. Higher temperature increases the rate of reaction but at the same time decreases the rate of absorption. Temperatures 30° C. or below cause a change in the reaction product with the formation of two liquid phases. A temperature of 35° C. was selected as the practical operating temperature for the absorber.

It will be noticed from the chlorine depletion data (Table I, Appendix B) that the reaction is a slow one. Consequently, the amount of reaction taking place in the tower proper is small. The amount of tower reaction has been generalized on the basis of data taken from the pilot unit. A rounded value of 15% of the total reaction has been ascribed to the tower and is to be used throughout all of the present evaluation study.

The tower itself can be treated as a chlorine absorber with the 15% reaction entering into the material balance equations. In order to decrease the work involved the log-mean method of calculating the number transfer units can be used. This simplification was shown to be justified in calculations made on the pilot absorber.

The equation for the usual graphical method of calculating the number of transfer units is (Perry's Handbook, page 1147):

$$N_t = \int_{y_2}^{y_1} \frac{dy}{(y-y^*)}$$

This equation can be simplified to the log-mean form as follows:

$$N_t = \int_{y_2}^{y_1} \frac{dy}{\Delta y_m} = \frac{1}{\Delta y_m} \int_{y_2}^{y_1} dy = \frac{y_1 - y_2}{\Delta y_m}$$

Δy_m = log-mean driving force

$$\Delta y_m = \frac{\Delta y_1 - \Delta y_2}{\ln \frac{\Delta y_1}{\Delta y_2}}$$

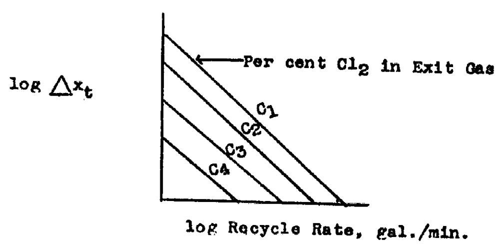
$$\Delta y_1 = y_1 - y_1^*$$

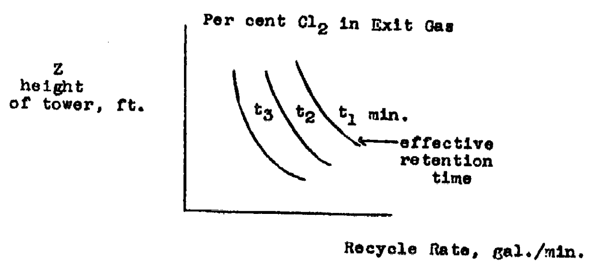
$$\Delta y_2 = y_2 - y_2^*$$

The tower should be designed to operate at a liquid velocity equal to 75 per cent of flooding. See data presented in Perry's Handbook, p. 1206, Fig. 41. (Note: The velocities should be in feet per second instead of feet per hour as erroneously defined at bottom of page 1205.) Some additional data are supplied in Table IV Appendix B for the physical constants of tower packing. For tower diameters between 12 in. and 36 in. use one-inch Raschig rings.

The equivalent H_t for the plant tower is translated from 1/4 inch Berl saddles to one-inch Raschig rings on the basis of equivalent area.

The following types of graphs will be found helpful in running off the multiple series of calculations required:





Retention System

The absorption tower is responsible for the physical absorption of chlorine and for 15 per cent of the total chlorine reacted. The remainder of the reaction must take place in an external system which provides the necessary retention time. Consideration should be given to short-circuiting in this system: "The Theory of Short-Circuiting" by R. B. MacMullin and M. Weber, Trans. A.I.Ch.E. 31, 409 (1934-35).

The reaction produces hydrogen chloride gas which muct be equalized with the feed gas to the absorption tower. It is to be assumed that one mol. of hydrogen chloride is produced for every mol of chlorine reacted.

It is suggested that the overall material balance equations should include a variable which expresses the work done by the retention system:

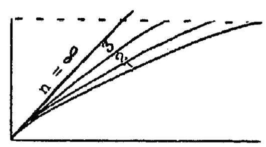
Δx_t = the reduction in free chlorine concentration due to chemical reaction with the PCA while passing through the retention system during an effective retention time of t minutes.

It is also suggested that a cross-plot of the retention data be made in which X_o (the chlorine concentration of the liquid entering the retention system) is plotted as ordinate against Δx_t as abscissa for effective retention times from 0 to 50 minutes, in increments of 5 minutes.

The graph on page 422 of MacMullin's article can be used to calculate the effective retention time (ERT) for various assumed values of the design retention time (DRT) in a system with a given number of tanks (n) while holding X_o constant.

The data can be summarized in tables for X_o = .002, .004, .006, .008, and .010 or plotted in graphs of the following nature:

log ERT, min.



log DRT, min.

$X_o = .002$

The combination of size and number of tanks which is most economical can be determined according to one of the problems listed in "Applications" of the MacMullin article. The determination is based on the relationship that the price of the tank varies as the 2/3 power of the volume.

The actual volume calculated from the recycle rate and the effective retention time should be used in the determination of the annual operating expense. The final design for the optimum conditions should assume a 75% working volume before a standard size tank is selected.

<u>Recycle Cooler</u>

The heat generated during the reaction is to be removed by a brine-cooled heat exchanger so that the column is maintained at an average temperature of 35° C.

Economic Analysis

The cost data should be plotted to show the variation of the total capital expenditure, the annual gross savings, the annual operating cost, the net annual savings, and the per cent return on the capital expenditure with the per cent chlorine in the exit gas. It is suggested that the range between 0.5 and 10 per cent chlorine in the exit gas, inclusive, be considered in estimation of costs and savings on the basis of data supplied in Appendix C.

Appendix A

PHYSICAL AND CHEMICAL DATA

I. Thermal Data for Partially Chlorinated Alcohol (PCA)

Specific Heat (liq.) at 35° C.	0.6
Specific Heat (gas) at 35° C.	0.4
Heat of Solution at 35° C.	450 Btu/lb. HCl
Heat of Reaction at 35° C.	2010 Btu/lb. Cl_2
Heat of Vaporization	183 Btu/lb.

II. Physical Data for PCA

Ave. Molecular Wt.	70
Specific Gravity 30° C./30° C.	1.100
Boiling Point (free of HCl and Cl_2)	83° C. at 760 mm. 35° C. at 125 mm.
Viscosity at 20° C.	11.0 Centistokes
Ethyl Chloride in PCA	0.05 lb./lb. PCA
The average concentration of hydrogen chloride in liquid film of condenser	24.8 per cent (wt.)
Molecular Volume	70.8

III. Reaction Data for PCA

Alcohol Requirement	0.55 lb. Cl_2/lb. 2B Alcohol
Hydrogen Chloride Produced	0.51 lb. HCl/lb. Cl_2 Reacted
Volume Increase	1.2 gal. PCA/gal. 2B Alcohol
Conc. of HCl in PCA (35° C.)	23.5 per cent (wt.)
Column Reaction	15 per cent of total

IV. Off-Gas Data

Rate	150 cu. ft./min. (3 lb./sq.in. gage and 70° F.)
Composition (Vol.)	75 per cent Hydrogen Chloride 15 per cent Chlorine 10 per cent Ethyl Chloride

Appendix B

ENGINEERING LABORATORY DATA

I. Free Chlorine Depletion in Partially Chlorinated Alcohol (Sp. Gr. 1.100 at 30°C./30°C.) at 35° C.

Time minutes	Free Chlorine weight per cent
0	1.114
8	0.800
10	0.628
14	0.510
17.5	0.418
24	0.283
34	0.152
44.5	0.065
54	0.0047

II. Pseudo Equilibrium of Chlorine and Partially Chlorinated Alcohol (Sp. Gr. 1.100 at 30°C./30°C.) at 35° C.

Free Cl_2 in PCA (x) Mol. Per cent	Free Cl_2 in Gas (y) Mol. Per cent
0.35	5.9
0.55	8.9
0.83	12.9
1.09	16.2
1.32	19.5
1.54	22.4

III. Height of Transfer Unit

Size: 30 mm. I.D. x 100 mm.
Packing: 1/4" Berl Saddles
Temperature: 35° C. (average)
Feed gas: 15 per cent Cl_2 with remainder HCl
Recycle PCA: Sp. Gr. 1.100 (30°C./30°C.)
Make-up: Ethanol (Formula 2B)

$\left(\frac{m_2G_2}{L_2}\right)$*	H_t (log-mean method) inches
0.178	9.1
0.571	12.2
1.04	15.7
1.53	19.2
1.79	21.5

* Conditions at dilute end of column

m_2 = slope of equilibrium curve

G_2 = molar gas flow

L_2 = molar liquid flow

IV. Packing Characteristics

Knight-ware	w	a'	F_w
1/4-in. Berl saddles	60	274	0.58
1-in. Raschig rings	45	58	0.68

w = weight, lb. per cu. ft. packing

a' = area, sq. ft. per cu. ft. packing

F_w = Fraction voids

Appendix C

COST DATA

I. Tanks - Suitably Baffled to produce efficient mixing.

Material	Cost for one 1000-gal. tank
Carbon steel	$550
Stainless steel	1600
Glass lined	1100
Rubber lined	950

Available in standard sizes, gal.

100, 200, 300, 500, 750, 1000, 1500, 2000, 3000, 5000, 10,000

Assume that the cost of each standard tank varies as $(\text{volume})^{2/3}$.

II. Towers

Diam., in.	6	12	18	24	30
Straight Sections, per foot					
Carbon steel	$31	$33	$36	$40	$45
Stainless steel	←	3 x carbon steel			→
Porcelain	45	70	100	135	180
Karbate	←	2 x porcelain			→
Top or Bottom Heads, each					
Carbon steel	25	27	30	34	39
Stainless steel	←	3 x carbon steel			→
Porcelain	40	60	85	115	150
Karbate	←	2 x porcelain			→

III. Tower Packing - one-inch Raschig Rings

Porcelain	$5 per cu. ft.
Carbon	$9 per cu. ft.

IV. Pumps - with explosion-proof motors

Carbon steel centrifugal 50 gpm, 30 ft. Head = $175
For rates of discharge other than 50 gpm, add or subtract $1 per gpm difference, and $1/2 per ft. of head for variation from 30 ft.

Stainless steel centrifugal	= 2 x carbon steel
Rubber diaphragm	= 6 x carbon steel
Glass centrifugal	= 3 x carbon steel

Assume that pumping head = 2 x tower height
Assume overall pump and motor efficiency is 50 per cent

V. Heat Exchangers

	Cost, Dollars per sq. ft. Area.				
Area, sq. ft.	50	100	200	300	500
Karbate	36	29	23	18	14
Pyrex	12	12	12	12	12
Glass Lined	25	25	25	25	25
Carbon Steel	10	7	5	4	3
Stainless Steel	20	14	10	8	6

U* overall coefficient of Heat Transfer, B.t.u./(hr.)(sq.ft.)(°F.)

Material	LIQ/ LIQ	GAS/ LIQ
Karbate	55	5
Pyrex	20	5
Glass Lined	15	5
Carbon Steel	50	5
Stainless Steel	50	5

* LIQ/LIQ 2 ft./sec. liquid rates
GAS/LIQ 30 ft./sec. gas rate

VI. Instrumentation 10% of installed cost of equipment

VII. Installation

Labor = 50% purchase price of equipment
Materials = 50% " " " "

VIII. Operating Time 365 days per year

IX. Labor $1.50 per man-hour

X. Depreciation Estimated life is 5 years for process equipment and 10 years for refrigeration equipment.

XI. Insurance, taxes, and interest 10% installed cost of equipment per year

XII. Maintenance

Labor 4 man hours per day at $2.00 per man-hour
Materials 10% installed cost of equipment

XIII. Other Overhead Expenses Assume 200 per cent of labor

XIV. Utilities

Steam	75¢/1000 lb.
Cooling water (80°F.)	2¢/1000 gal.
Electric power	1.1¢/kwh
Refrigeration (10°F. brine)	

Requirements per ton of refrigeration:

Cooling water	3 gal./min.
Power	2 hp.
Installed Cost	$800

XV. Chemicals

Alcohol (2B) 75.0¢/gal.
Lime (Dolomitic hydrate) 0.75¢/lb.
Basicity factor = 0.718 lb. CaO per lb. of lime
Use a 20% excess of lime
Chlorine 3.5¢/lb.
Tech. Muriatic Acid 20°Be 1.3¢/lb.

The net effect of the off-gas treatment is to reduce the amount of Cl_2 charged and to decrease the expense of neutralization at the waste disposal plant. The alcohol consumption is unaffected by this unit and no credit is to be taken for the HCl recovered from the off-gas.

Appendix D

NOMENCLATURE

Ref: See Chem. Eng. Progress, Vol. 43, March News Section, P. 45 (1947).

a' = surface per unit volume of packing square foot per cubic foot

°Bé = specific gravit unit, degree Baume

B.t.u. = unit of energy, British Thermal unit

¢ = unit of money, cent

c = mol fraction of chlorine in exit gas

°C. = temperature, degree Centigrade

cu. ft.= unit of volume, cubic foot

DRT = design retention time, minute

ERT = effective retention time, minute

°F. = temperature, degree Fahrenheit

ft. = unit of length, foot

F_w = fraction voids of tower packing

G = mass velocity of gas, mol per hour

gal.= unit of liquid volume, gallon

h = individual film coefficient, B.t.u./(hr.)(sq.ft.)(°F.)

hp. = unit of power, horsepower

hr. = unit of time, hour

H_t = height of transfer unit, "H.T.U.", inch and foot respectively for laboratory and plant tower

in. = unit of length, inch

L = mass velocity of liquid, mol per hour

lb. = unit of mass, pound

m = slope of equilibrium curve

min. = unit of time, minute

mm. = unit of length, millimeter

n = number of equal volume tanks in retention system

N_t = number of transfer units

PCA = partially chlorinated alcohol

RR = liquid recycle rate to tower, gal./min.

$ = unit of money, dollar

sec.= unit of time, second

Sp. Gr.= specific gravity

sq. ft.= unit of area, square foot

sq. in.= unit of area, square inch

t = assumed retention time, minute

U = overall coefficient of heat transfer, B.t.u./(hr.)(sq.ft.)(°F.)

w = unit weight of tower packing, pound per cubic foot

X = mol fraction of chlorine in liquid

X_o = mol fraction of chlorine in liquid entering retention system

ΔX_t = the reduction in free chlorine concentration due to chemical reaction with the PCA while passing through the retention system during an effective retention time of t minutes.

y = mol fraction of chlorine in gas

y* = pseudo equilibrium value of mol fraction chlorine in gas

Δy_m = logarithmic mean driving force

$$= \frac{\Delta y_1 - \Delta y_2}{\ln \frac{\Delta y_1}{\Delta y_2}}$$

$$\Delta y_1 = y_1 - y_1^*$$

$$\Delta y_2 = y_2 - y_2^*$$

Z = Height of packed tower, foot

Subscript 1 refers to conditions at point gas enters tower

Subscript 2 refers to conditions at point gas leaves tower (dilute end)