CONCENTRATION OF HEAVY WATER

by

Anh-Quang Nguyen

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ABSTRACT

A micro heavy water concentration unit using the G.S. process was constructed to study possible process improvements. The deuterium isotope exchange was performed successfully in this unit. It was found that the use of monoethanolamine (MEA) in conjunction with the G.S. process had little or no effect on the recovery fraction of heavy water from the feed. However, the experiments indicated that the gas rate could be increased to attain a higher production rate, or equivalently, for the same production rate the size of the towers could be slightly reduced.

The improvement was found only marginally attractive particularly because one more stage could be needed to recover the MEA which was introduced in the feed water.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. W. Hayduk for his valuable assistance and direction in this work.

He also wishes to thank Mr. G. Gasperetti, Mr. D. Roy and Mr. A. Bonaldo for their aid in constructing the equipment.

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NOMENCLATURE

B_1, B_2	second virial coefficients of pure component 1 and pure component 2
B_m	second virial coeficient of a gas mixture
B_{12}	cross coefficient defined by equation (15)
d_g	gas mixture density
F	feed rate, lb mole/day
G	gas rate, lb mole/day
H	humidity, mole water/mole H_2S gas
K_o	equilibrium constant for the reaction $H_2O + D_2O \rightleftharpoons 2\ HDO$
K_x	equilibrium constant for the reaction $H_2O_\ell + HDS_\ell \rightleftharpoons HDO_\ell + H_2S_\ell$
L	liquid rate, lb mole/day
P	pressure, psia (atm in equation 12)
P^o	vapor pressure, mm Hg
P'	production rate, lb mole/day
S	solubility of H_2S, mole dissolved H_2S/mole liquid
T	temperature, ^oK (^oC in equation 24)
T_h	hydrate temperature, ^oC
x	D atom fraction in the liquid phase
X	D to H ratio in the liquid phase
y	D atom fraction in the gas phase
Y	D to H ratio in the gas phase

x_1	mole fraction of component 1 in the liquid phase
y_1	mole fraction of component 1 in the gas phase
Z_m	compressibility of the gas mixture
α_x	relative volatility of HDO to H_2O in the liquid phase
β	overall separation factor

Subscript

1,2	refer to components 1 and 2
c,C	refer to the cold tower
g,y	refer to the gas phase
h,H	refer to the hot tower
ℓ,x	refer to the liquid phase
m	refers to the mixture

Constants

Equation (2):

$T = {}^{o}K$

$A = 3.7621$

$B = 1.5057 \times 10^{-3}$

$C = 4.0 \times 10^{-6}$

Equation (7):

y = mole H_2O vapor/ mole gas mixture

$T = {}^{o}K$

P = psia

$A = 9.6689$	$E = 0.056442$	$J = 7.6273 \times 10^{-6}$
$B = 9.1243$	$F = 6.8678 \times 10^{-5}$	$K = 9.5097 \times 10^{-10}$
$C = 0.85231$	$G = 1.8741 \times 10^{-8}$	
$D = 0.02829$	$H = 0.023154$	

Equation (8):

x = mole dissolved H_2S/mole solution

$T = {}^oK$

P = psia

$A = 5.0375$

$B = 0.01128$

$C = 2.0071 \times 10^{-5}$

$D = 1.5586 \times 10^{-8}$

$E = 0.044033$

$F = 5.7530 \times 10^{-6}$

$G = 8.027 \times 10^{-8}$

Equation (9):

$A = 0.066875$

$B = 1.4866 \times 10^{-4}$

$C = 6.119 \times 10^{-8}$

$D = 3.4556 \times 10^{-4}$

$E = 4.5473 \times 10^{-7}$

$F = 2.6892 \times 10^{-7}$

$G = 3.3587 \times 10^{-13}$

Equation (12):

P = atm

$T = {}^oK$

$B_o = 0.5250302$

$B_1 = 665.3158$

$B_2 = -3.461192 \times 10^5$

$B_3 = 7.928513 \times 10^7$

$B_4 = -6.75079 \times 10^9$

$B_5 = 4.016812$

$B_6 = -4.233719 \times 10^3$

$B_7 = 1.335203 \times 10^6$

$B_8 = -1.937060 \times 10^8$

$B_9 = 1.089689$

$B_{10} = -1.230729 \times 10^3$

$B_{11} = 4.594888 \times 10^5$

$B_{12} = -5.671054 \times 10^7$

$B_{13} = -3.537612 \times 10^{-2}$

$B_{14} = 39.17374$

$B_{15} = -1.423831 \times 10^4$

$B_{16} = 1.692439 \times 10^6$

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INTRODUCTION

Heavy water (D_2O) is used as the moderator in the CANDU reactors. A forecast of Canadian heavy water production rate shows an increase to about 4000 tons/yr in 1980 (1) from 1000 tons/yr in 1975. CANDU reactors require an inventory of approximately 0.8 Mg of heavy water per MW(e) capacity. Subsquent make-up requirements are negligible, much less than one percent per year. The concentration of heavy water in natural water is approximately one part in 7000. Fresh water generally has a lower deuterium content compared to ocean water. There is considerable variation in deuterium content in natural water due to isotopic fractionation in natural processes.

Because of its low concentration, heavy water occurs mainly in the monosubstituted form, i.e. HDO.

$$H_2O + D_2O \rightleftharpoons 2\ HDO$$

The equilibrium constant K_o is defined as follow:

$$K_o = \frac{[HDO]^2}{[H_2O][D_2O]} \qquad \ldots (1)$$

It was found that K_o varies with temperature (2) according to the following equation in which A, B, and C are numerical constants whose values are listed in the Nomenclature section:

$$K_o = A + BT - CT^2 \qquad \ldots (2)$$

Figure 1 shows K_o as a function of temperature.

Because of its low concentration the separation of heavy water from natural water by distillation cannot be performed readily. Most physical properties of light water and heavy water are very similar (Table 1).

The present cost of heavy water in Canada is $70/kg and is predicted to go up as high as $100/kg by 1980. At this level, the cost of heavy water will contribute an equivalent of nearly 15% of the total cost for a CANDU nuclear power plant. Therefore it is desirable to develop new processes or to improve present processes to produce heavy water at a lower cost.

Some potential chemical exchange processes for the production of heavy water will be briefly described.

1) The monothermal low-pressure water-hydrogen exchange process involves the chemical exchange reaction:

$$H_2O + HD \rightleftharpoons HDO + H_2$$

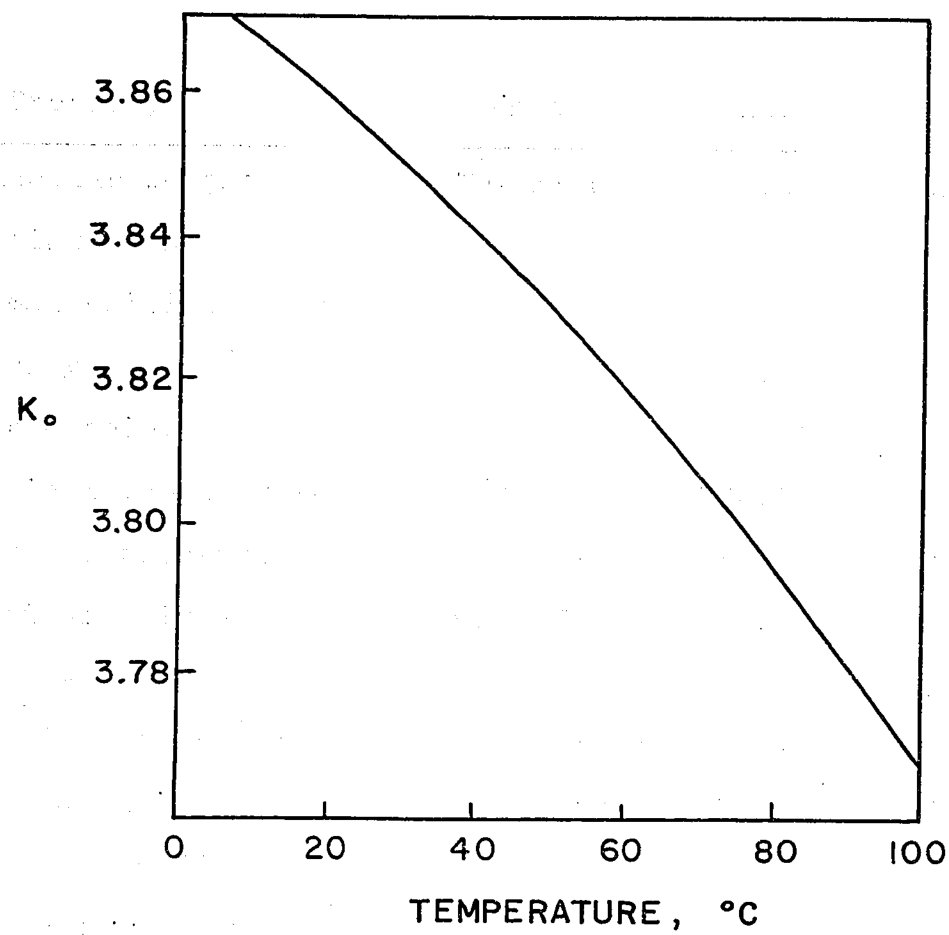


Figure 1. EQUILIBRIUM CONSTANT, K_o FOR THE REACTION: $H_2O + D_2O \rightleftharpoons 2\ HDO$

Table 1. Some significant physical properties of light water and heavy water.

Property	Unit	H_2O	D_2O
Molecular weight	^{12}C scale	18.015	20.028
Melting point	^oC	0.00	3.81
Normal boiling point	^oC	100.00	101.42
Density at 25 ^oC	g/cm^3	0.9970	1.1044
Triple point	^oC	0.01	3.82
Critical temperature	^oC	374.1	371.1
Critical pressure	atm	218.3	215.9
Critical volume	cm^3/mole	55.3	55.0
H_{vap} at 25 ^oC	kcal/mole	10.52	10.85
C_p (liq. at 25 ^oC)	cal/deg mole	17.99	20.16
C_v (liq. at 25 ^oC)	cal/deg mole	17.80	20.0
S_{vap} at 25 ^oC	eu	28.39	29.22
Refractive index, n_D^{20}		1.3330	1.3283
Viscosity at 25 ^oC	cP	0.890	1.107
Surface tension at 25 ^oC	dyne/cm	71.97	71.93

The water-hydrogen exchange process was used in conjunction with electrolysis in the Trail plant, B.C. (3) Deuterium was exchanged between water and hydrogen gas by means of a steam-hydrogen exchange in catalyst beds consisting of platinum on active charcoal suspension which alternated with bubble-cap trays where steam and water were equilibrated. Enriched water was converted to hydrogen by electrolysis and the depleted hydrogen was used for ammonia synthesis. This process is no longer attractive because of the large amount of catalyst required and the low operating pressure. The production is limited to a few locations where ammonia is manufactured from electrolytic hydrogen.

2) The ammonia-hydrogen exchange process involves the following exchange reaction:

$$NH_3 + HD \rightleftharpoons NH_2D + H_2$$

Despite the technical problems, the ammonia-hydrogen exchange process has the potential advantage of having a high separation factor (Figure. 2)(4). There are two ways in which the NH_3/H_2 exchange reaction may be utilized for heavy water production, namely, by a monothermal process or a bithermal process. Both processes require a liquid phase catalyst (potassamide). It is significant that the

Murphree point efficiency of a bubble slot at -40 ^{o}C, the operating temperature of the cold tower, is only 0.5 percent (5). A very low cold tower temperature is necessary to avoid excessive plant volume. Even though the energy requirement of the bithermal process is substantially lower than for the monothermal one (6), the choice between the two depends mainly on the cost associated with contactors operating at the low temperature.

3) The H_2S/H_2O dual temperature exchange process is the Girdler-Spevack or G.S. process. This process will be described in detail in the following section.

There are many more possible heavy water processes (7), but most of these have not been studied in any detail.

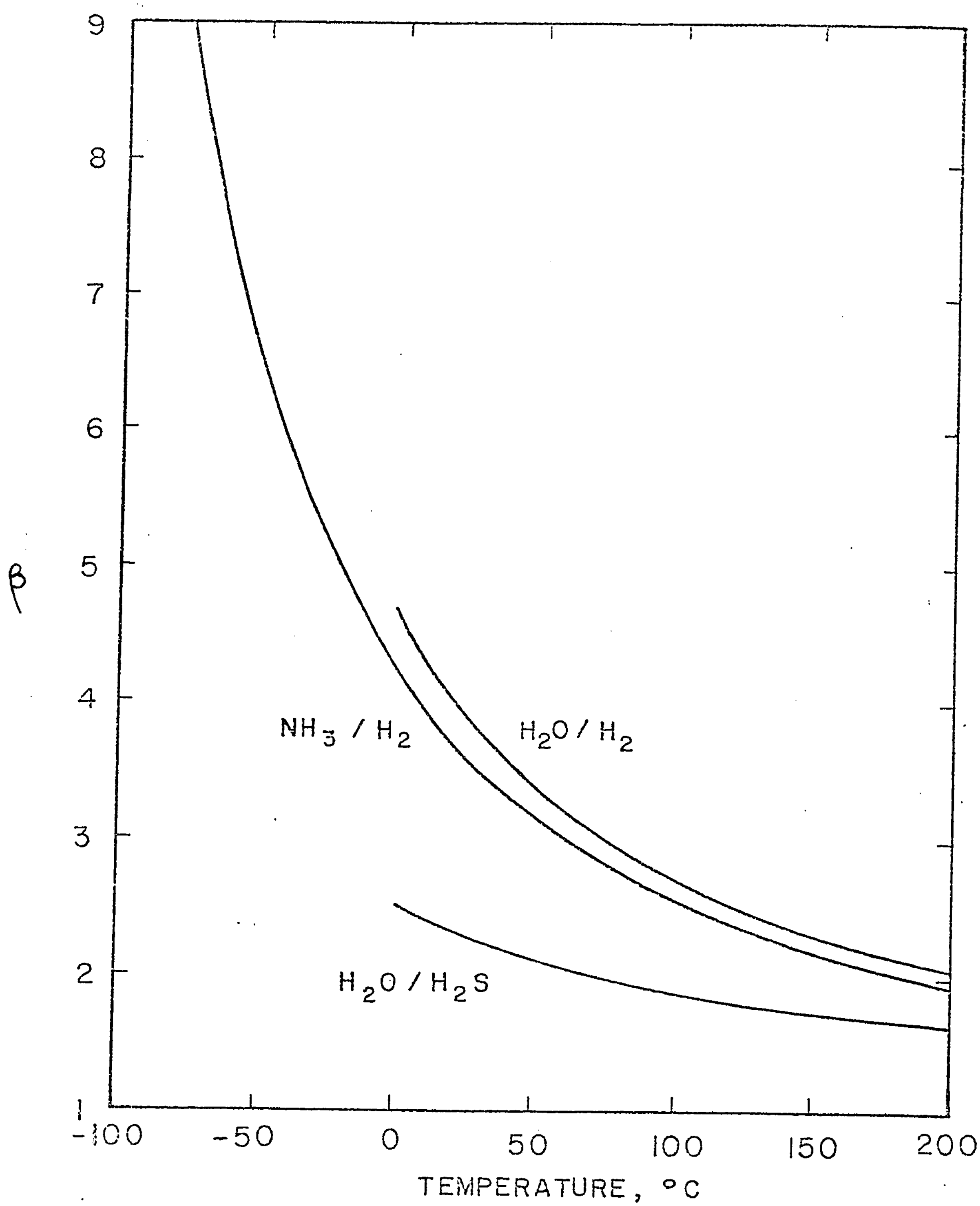


Figure 2. SEPARATION FACTOR FOR CHEMICAL EXCHANGE

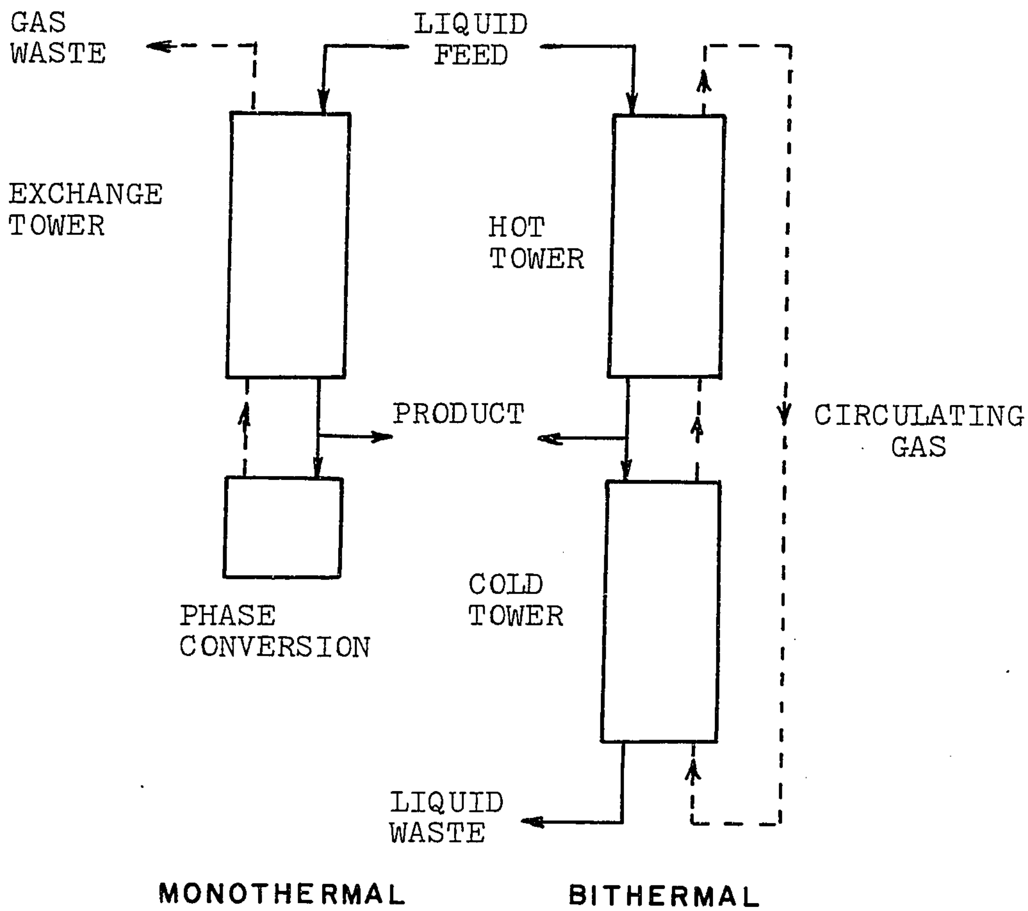


Figure 3. MULTISTAGE CHEMICAL EXCHANGE

THE GIRDLER-SPEVACK PROCESS

A. Principle of the G.S. process:

The G.S. process has been utilized in North America to produce heavy water. In Canada the first G.S. heavy water production plant was constructed in the early 1960's at Glace Bay, N.S. by Deuterium of Canada Ltd. The Bruce heavy water plant, which is owned by Ontario Hydro, is presently the world's largest heavy water production facility. A $1.5 billion program is underway to build more units.

The G.S. process is based on the following reaction:

$$H_2O_\ell + HDS_\ell \rightleftharpoons HDO_\ell + H_2S_\ell$$

The above reaction occurs in the liquid phase between water and dissolved hydrogen sulfide. The equilibrium constant for the deuterated species in the liquid phase is given by:

$$K_x = \frac{[HDO]\,[H_2S]}{[H_2O]\,[HDS]} \qquad \ldots (3)$$

K_x varies considerably with temperature as shown in figure 4 (8), and it is this variation that provides the

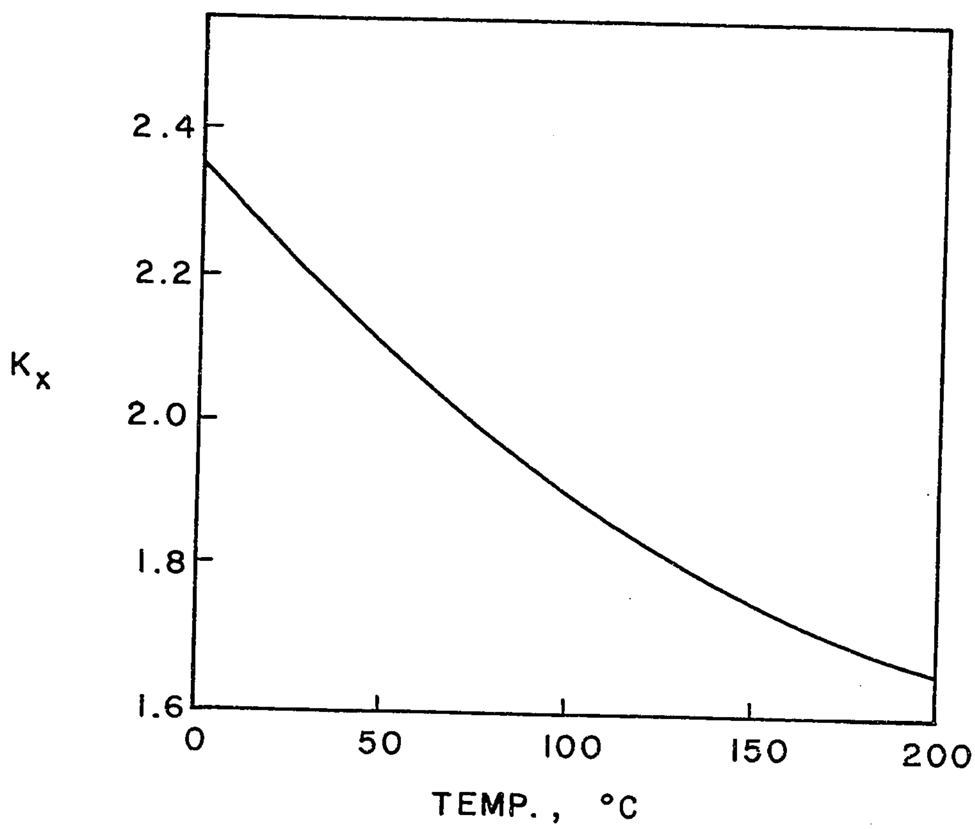


Figure 4. EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT FOR THE LIQUID PHASE EXCHANGE OF DEUTERIUM BETWEEN DISSOLVED H_2S AND WATER.

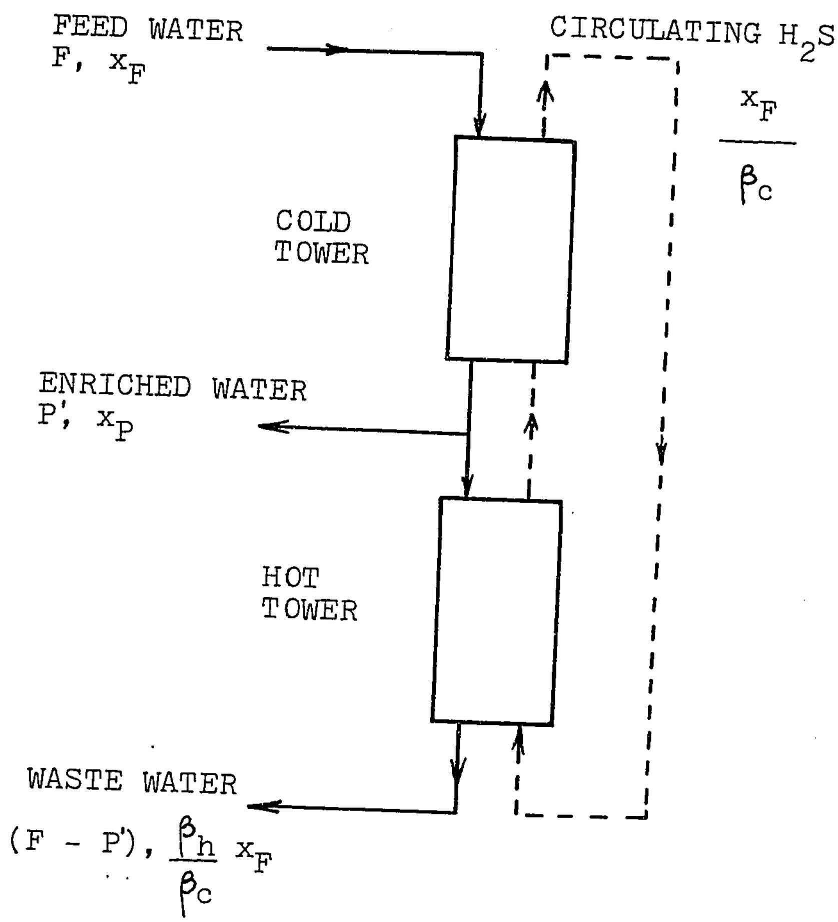


Figure 5. SIMPLIFIED PROCESS FLOW DIAGRAM FOR THE G.S. PROCESS.

the basis for the separation achieved in the process.

The basic process flow diagram for the H_2S/H_2O exchange is shown in figure 5. Feed water is passed downward through the cold tower, countercurrent to H_2S gas at a pressure of about 275 psig. Water is progressively enriched in D_2O as it flows through the hot tower. Enriched water is withdrawn from the bottom of the cold tower. The operating conditions chosen represent approximately the economic optimum for the system. The optimum conditions depend mainly on the physical properties of aqueous hydrogen sulfide solutions. Since K_x varies with temperature it is desirable to achieve the largest possible difference between the temperature of cold and hot towers. A high pressure in the towers permits high mass flow rates of gas without excessively large tower diameters. The upper limit of pressure is that at which H_2S liquefies or its solid hydrate forms at the cold tower temperature. The optimum temperature for the hot tower is not as well defined, but above the 140-150 ^{o}C range the potential gains from an increase in temperature are more than offset by the rapid increase in the concentration of water in the gas phase. The calculations for fractionation and absorption efficiency and recovery are similar to those for distillation and the more usual gas absorption processes. At the operating conditions of the G.S. process, the humidity of the gas and the solubility of H_2S in the liquid cannot be ignored. An overall separation factor can be calculated based on the isotopic content of both gas and liquid phases. The separation factor expresses the overall relation between the concentration of deuterium in the gas phase both as HDS and as HDO vapor, to that in the liquid phase, as HDO and dissolved HDS.

By definition:

$$\beta = \left.\frac{x(1-y)}{y(1-x)}\right|_{\text{equilibrium}} \qquad \ldots (4)$$

It follows that for low deuterium content solutions:

$$\beta = \left.\frac{x}{y}\right|_{\text{equilibrium}} \qquad \ldots (4a)$$

Based on the assumption that an infinite number of plates are available in each of the towers, it may be considered that equilibrium is attained at the extremities. The circulating H_2S leaving the top of the cold tower would then have a deuterium concentration of x_F/β_c, where x_F would represent the deuterium concentration in the feed stream and β_c the overall separation factor in the cold tower. The water leaving the bottom of the hot tower, considered to be at equilibrium with the entering gas, would therefore have a concentration $\beta_h x_F/\beta_c$, where β_h would be the overall separation factor in the hot tower. The mass isotope removed from the water would then be:

$$P'x_P = Fx_F - (F-P')\beta_h x_F/\beta_c \qquad \ldots (5)$$

Since P', in an actual operating isotope separation plant, is very small when compared with F, the above expression approximates to:

$$P'x_P = x_F F\left(1-\frac{\beta_h}{\beta_c}\right) \qquad \ldots (6)$$

Hence the maximum fraction of isotope in the feed that is recoverable by enrichment is: $\left(1-\frac{\beta_h}{\beta_c}\right)$ ... (7)

A typical heavy water production plant has 4 or 5 stages each of which consists of two to four pairs of hot and cold towers in parallel, with each tower having a diameter of up to 15 ft. As an example, the G.S. unit at the Dana plant, U.S.A. has five stages. In the cold tower circuit cold water passes over a total of 350 bubble-cap trays in series to eventually produce water containing 15-20% deuterium. There are a similar number of trays in the hot towers. Because of the increased isotope concentration the second stage towers have smaller cross section areas.

Based on the Savannah River plant, U.S.A., for every pound of D_2O produced it takes 40,000 lb of feed water for which the isotope recovery fraction is approximately 18%, 6000 lb of steam at 250 psig, and 1500 gal of cooling water at 85 ^{o}F. The heavy water product from the G.S. units is upgraded to 99.75 wt% D_2O by vacuum distillation. A series of two or three distillation towers operating at a temperature range of 130-150 ^{o}F and a pressure range of 120-180 mm Hg is usually furnished for this purpose.

B. Physical and thermodynamic properties of aqueous-heavy water-H_2S solutions

Only those properties needed in the presentation of the process concerned in this work will be discussed. Additional properties (both physical and thermodynamic) can be obtained from reports by Galley et. al.(2) and Elliott J.N.(9).

1. Vapor-liquid equilibrium compositions for the H_2O-H_2S system.

Selleck et. al.(10) measured equilibrium compositions of both phases over a wide range of temperatures and pressures. Burgess and Germann(11) derived equations to fit these data.

a) The mole fraction of water vapor in the water vapor-H_2S gas mixture was expressed by the following equation:

$$\ln y = -A - B(\ln P) + C(\ln P)^2 - D(\ln P)^3 + E(T) + G(T)^3 - F(T)^2 + H(T)(\ln P) - J(T)^2(\ln P)^2 + K(T)^3(\ln P)^3 \quad \ldots (7)$$

This equation fit most of Selleck's data to within 1%.

b) Solubility of H_2S in water:

Burgess used two equations for two different temperature ranges:

(i) For temperatures from the hydrate point to 100 °C:

$$\ln x = A + BP - CP^2 + DP^3 - ET + FT^2 + GT^3 \quad \ldots (8)$$

(ii) For the temperature range from 100 °C to 171 °C:

$$x = -A + BP - CP^2 + DT - ET^2 - FPT + GP^2T^2 \quad \ldots (9)$$

The solubility of H_2S in water has also been reported by Clarke and Glew (12) in the temperature range 0-50 °C, and by Wright (13) in the vicinity of the hydrate point. These latter data are less important for the G.S. process which employs high operating pressures and a wide temperature range.

2. Density of water saturated with H_2S gas:

It is assumed that the density of water is not significantly affected by the presence of H_2S. The maximum amount of H_2S present in an H_2S-saturated water solution is about 0.032 mole fraction or 6% by weight at 87 ^oF and 36 psia. The ideal solution density could be calculated based on water and liquid H_2S densities at the maximum solubility to be 61.3 lb/ft^3 which is 1.4% less than the water density at that temperature. It appears that any error caused by assigning the density of water to all aqueous-H_2S solutions was not serious.

3. Densities of H_2S-water vapor gas mixtures:

The molecular weight and density of the gas mixtures were estimated using the following equations:

$$MW_m = 18.02\ y_{H_2O} + 34.08\ y_{H_2S} \qquad \ldots (10)$$

$$d_g = \frac{P\ MW_m}{Z_m RT} \qquad \ldots (11)$$

4. Specific volume of dry H_2S gas:

The volumetric behaviour of dry H_2S was reported by West (15). The experimental data extend from -76 ^{o}F to 1300 ^{o}F and up to a maximum pressure of 1030 psi. The specific volume of H_2S was calculated by Burgess (11) using the Beattie Bridgeman equation in the virial form. The calculation involved trial and error methods. Other P-V-T data were also reported by Reamer et. al. (16). Galley et. al. (2) fitted these data to an equation of state in the virial form explicit in Z, the compressibility factor. The errors were less than 0.25%.

$$\begin{aligned} Z = B_o &+ \frac{B_1}{T} + \frac{B_2}{T^2} + \frac{B_3}{T^3} + \frac{B_4}{T^4} \\ &+ \frac{B_5 P}{T} + \frac{B_6 P}{T^2} + \frac{B_7 P}{T^3} + \frac{B_8 P}{T^4} \\ &+ \frac{B_9 P^2}{T} + \frac{B_{10} P^2}{T^2} + \frac{B_{11} P^2}{T^3} + \frac{B_{12} P^2}{T^4} \\ &+ \frac{B_{13} P^3}{T} + \frac{B_{14} P^3}{T^2} + \frac{B_{15} P^3}{T^3} + \frac{B_{16} P^3}{T^4} \qquad \ldots (12) \end{aligned}$$

5. Volumetric properties of water-saturated H_2S gas:

No accurate methods are available for estimating the specific volumes of mixtures containing polar components although two approaches have been recommended:

a) According to Reid and Sherwood (17) the compressibility factor of a polar mixture can be determined by using an equation of state in the virial form:

$$Z_m = 1 + \frac{B_m P}{RT} + (C - B)^2 \frac{P^2}{(RT)^2}$$

$$+ (D - 3BC + 2B)^3 \frac{P^3}{(RT)^3} + \cdots \qquad \ldots (13)$$

At low pressure, only the second virial coefficient is significant, so that as a good approximation:

$$Z_m = 1 + \frac{B_m P}{RT} \qquad \ldots (14)$$

For binary mixtures the second virial coefficient may be estimated from those of the pure components:

$$B_m = y_1^2 B_1^2 + 2y_1 y_2 B_{12} + y_2 B_2^2 \qquad \ldots (15)$$

The virial coefficients for the pure components and the cross coefficient can be determined from the Stockmayer potential.

b) Dalton's law adapted for gas compressibilities:

$$Z_m = Z_{H_2O}\, y_{H_2O} + Z_{H_2S}\, y_{H_2S} \qquad \ldots (16)$$

Galley et. al. (2) found good agreement between compressibilities estimated by the two methods. Listed in table 2 are compressibilities calculated using both methods.

Table 2. Compressibility fators for H_2S-water vapor mixtures

Temperature ^oC	Pressure psia	Z_m Stockmayer method	Z_m Dalton's law
37.7	300	0.830	0.845
60.0	300	0.883	0.882
93.3	300	0.903	0.916
148.8	300	0.940	0.948

6. Hydrate temperature:

The hydrate temperature is the one at which H_2S hydrate will form at a specified pressure. Burgess (11) derived the following equation to fit Selleck's data (10):

$$T_h = 9.3987 \ln P - 24.85 \qquad \ldots (17)$$

7. The overall separation factor:

As mentioned earlier, at low deuterium concentrations the overall separation factor may defined as follows:

$$\beta = \frac{x}{y} \qquad \ldots (18)$$

The change in concentration through a G.S. tower can be determined by a McCabe-Thiele-type diagram similar to that used for absorption. For low concentrations the equilibrium line can be considered straight with slope equal to $1/\beta$. The operating line has a slope equal to the ratio of liquid to gas flow rates (Figure. 6). The optimum situation is that in which the pair of operating lines is mathematically centered between the equilibrium lines. The significance is that the ratio of the slope of the equilibrium line to that of the operating line for the hot tower is equal to the reciprocal of that ratio for the cold tower. The difference between the slopes of the hot and cold tower operating lines is due primarily to the water vapor content of the hot gas. It is interesting to note that if the flow rates are at the optimum the concentration of D_2O at the middle tray of the cold tower will equal that at the middle tray of the hot tower. Hence control of the G.S. process is based on sampling and analysis at these points. Changes of gas or liquid flow rate of 0.5% can be detected and corrected for on the basis of the mid-column analyses (8). Burgess (18) developed a

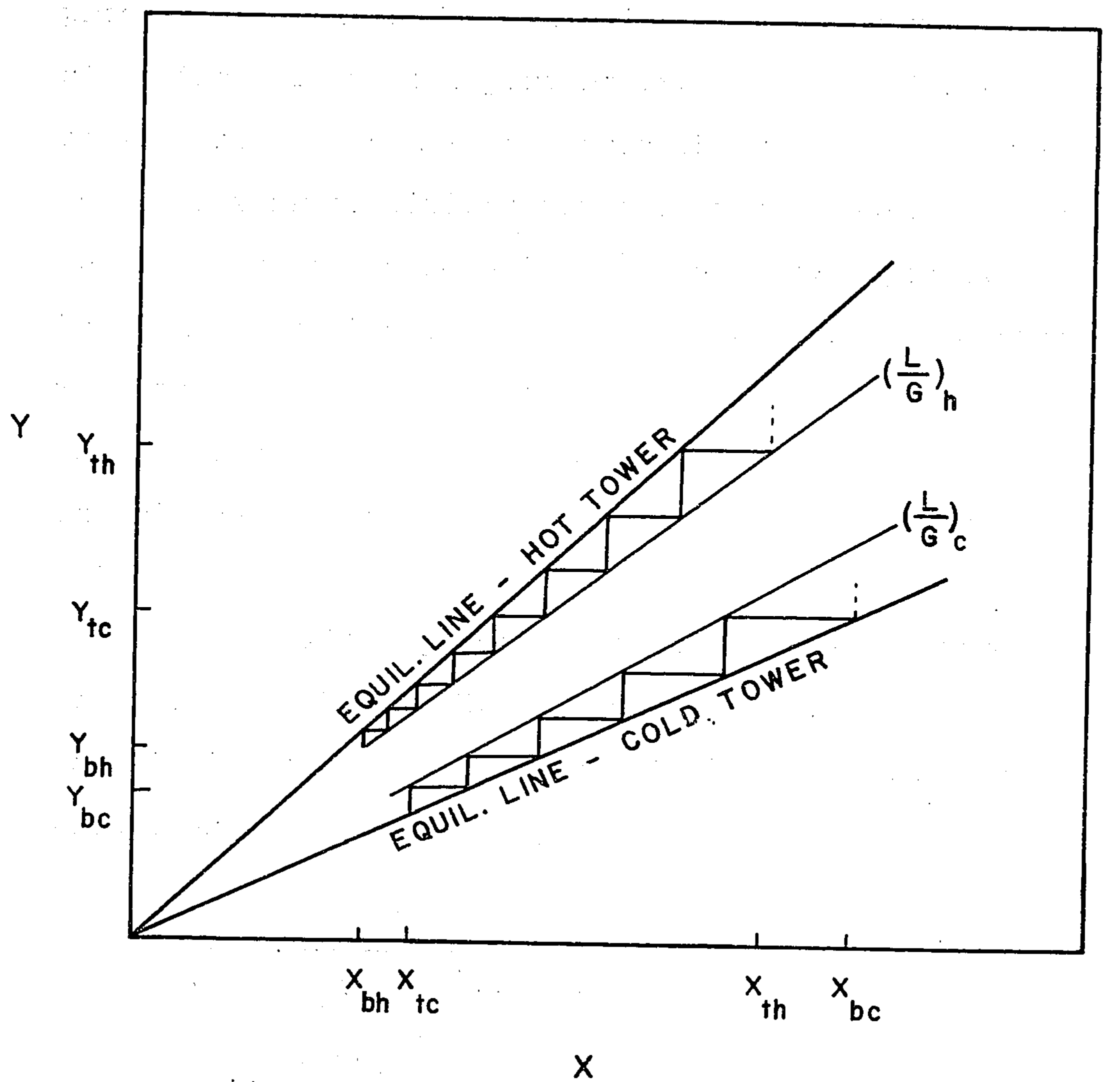


Figure 6. MC CABE-THIELE DIAGRAM FOR A TYPICAL PAIR OF FIRST STAGE G.S. TOWERS.

mathematical model which may be used to establish process set points for achieving production goals, to study the effect of important process variables on these goals, and to evaluate proposed changes in the design and operating conditions for the process equipment. The model was based on equations already developed by Bebbington and Thayer (8) but the appropriate equations were solved numerically by means of a digital computer. The results were found to agree generally with plant experience and some calculations using the McCabe-Thiele method.

The overall separation factor , the relative volatility of HDO to H_2O, α_x, and the liquid phase equilibrium constant K_x were calculated by means of equations given by Bebbington and Thayer (8) as follows:

$$\beta = \frac{(1 + H)\ (S + K_x)}{\alpha_x(1 + S)(1 + HK_x)} \qquad \ldots (19)$$

$$\alpha_x = \frac{[HDO]_g [H_2O]_l}{[H_2O]_g [HDO]_l} \qquad \ldots (20)$$

$$K_x = \left.\frac{[HDO]\ [H_2S]}{[H_2O]\ [HDS]}\right|_l \qquad \ldots (21)$$

The parameters α_x and K_x were determined experimentally at various temperatures and fitted by the exponential equations as follows:

$$\alpha_x = 1.1596\ e^{-65.43/T} \quad \ldots (22)$$

$$K_x = 1.01\ e^{233/T} \quad \ldots (23)$$

It may be observed that β varies slightly with the concentration of D_2O. The variation of β with deuterium concentration was reported by Galley et. al. (2) and is shown in table 3.

8. The effects of some process variables on the production rate:

The effects of temperature, gas rate, L/G on production rate as reported by Burgess (18) are graphically shown in figures 7 and 8.

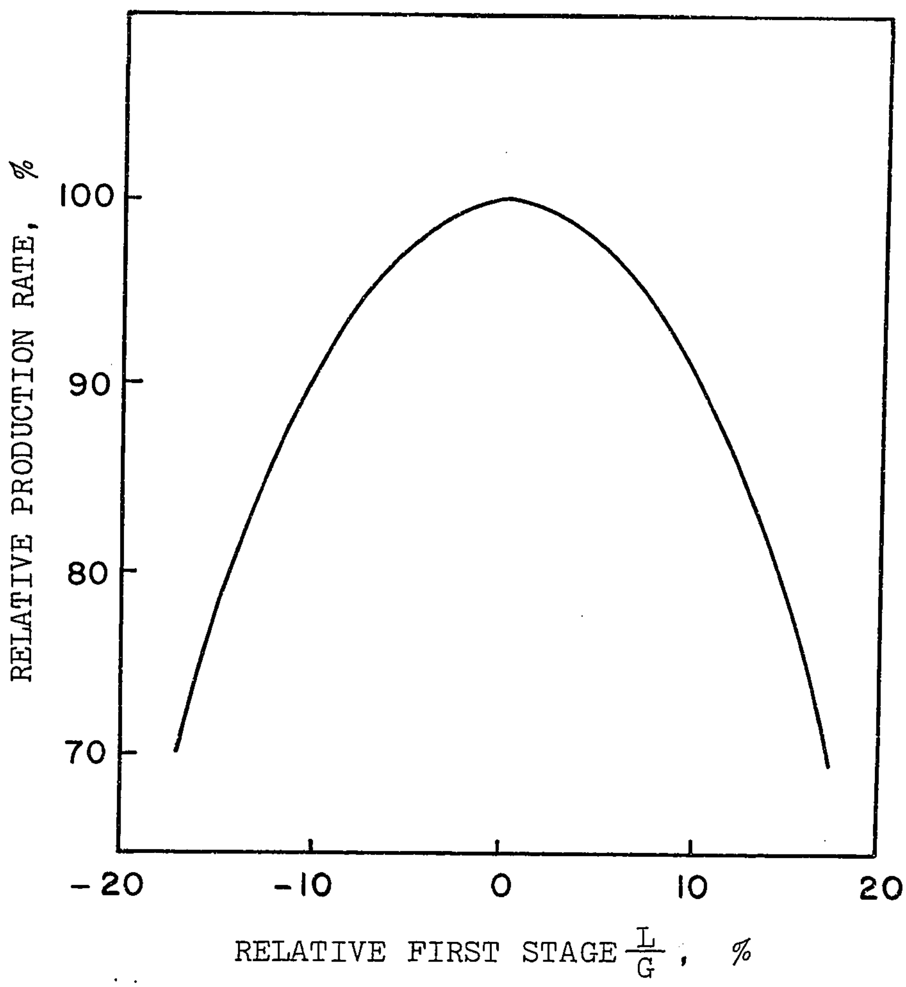


Figure 7. INFLUENCE OF LIQUID TO GAS RATIO IN THE G.S. PROCESS.

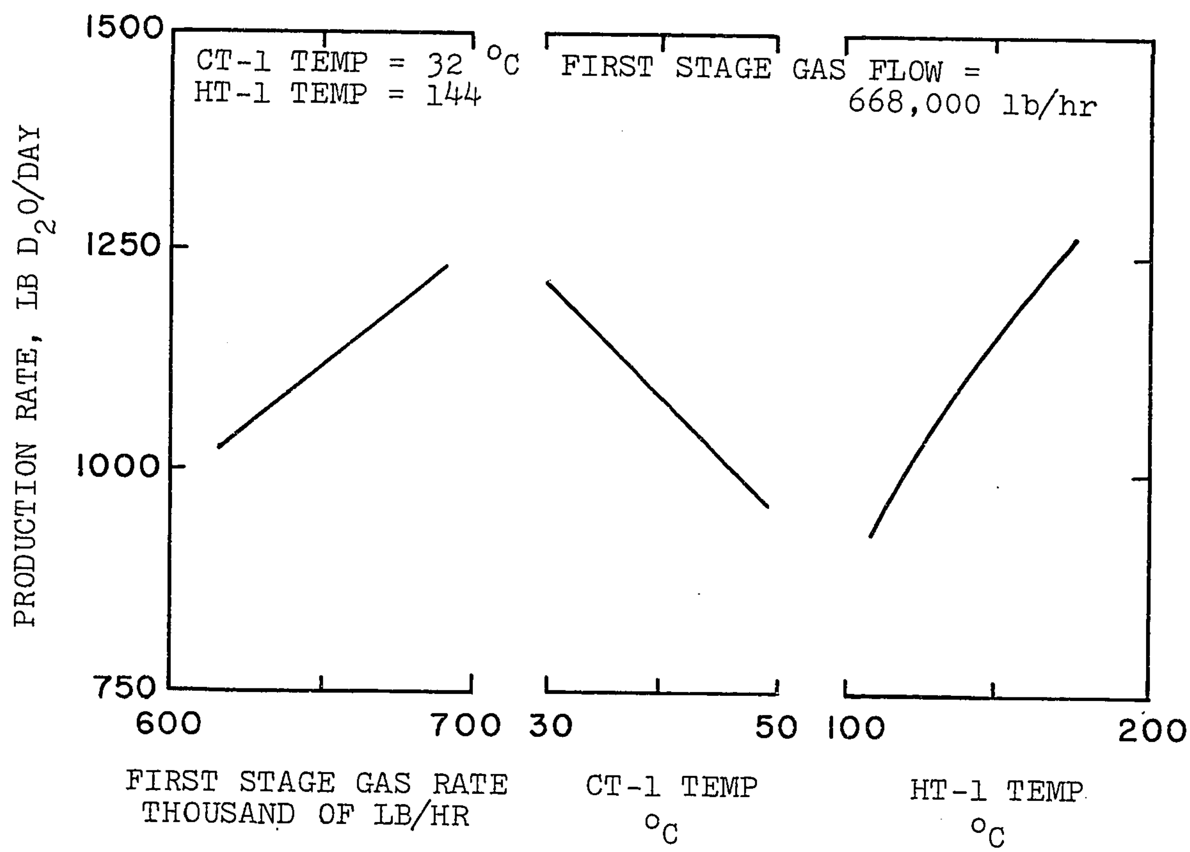


Figure 8. EFFECT OF GAS RATE AND OPERATING TEMPERATURE ON THE PRODUCTION RATE.

Table 3. Variation of the overall separation factor with deuterium concentration.

Pressure, psig	280	300
Temperature, ^{o}F	90	265
D/D+H	β_c	β_h
0.000158	2.2387	1.6991
0.000398	2.2388	1.6991
0.000631	2.2388	1.6991
0.001585	2.2389	1.6991
0.002512	2.2390	1.6991
0.003981	2.2392	1.6991
0.006310	2.2395	1.6991
0.010000	2.2400	1.6991
0.039811	2.2438	1.6991
0.100000	2.2515	1.6990
0.251189	2.2590	1.6980
0.398107	2.2892	1.6955
0.630957	2.3176	1.6880

MONOETHANOLAMINE AND THE G.S. PROCESS

Aqueous monoethanolamine solution has long been used in the chemical industries to strip acid gases such as hydrogen sulfide. Its capacity for acid gas is much greater than that of diethanolamine and triethanolamine (figure 9) (19). The capacities shown in figure 9 were based on 90% saturation at 95 ^oF and 25 psig, with a 25% safety factor.

1. Solubility of H_2S in aqueous MEA solutions:

The solubility of H_2S in 2.5 N and 5 N aqueous MEA solutions has been measured by Otto et.al.(20) over a wide range of temperature and pressure. Other workers (21)(22) also reported the solubility of H_2S in MEA solutions of various concentrations but most of the data were restricted to low pressures and temperatures. Figures 10, 11 and 12 show the solubility of H_2S at different MEA concentrations and temperatures.

Monoethanolamine solutions can combine with much more H_2S gas than water alone could, therefore, by introducing MEA into the G.S. towers the capacity of the liquid for the H_2S and HDS constituents would be increased. MEA could be recovered readily by distillation.

2. Vapor-liquid composition of MEA solution:

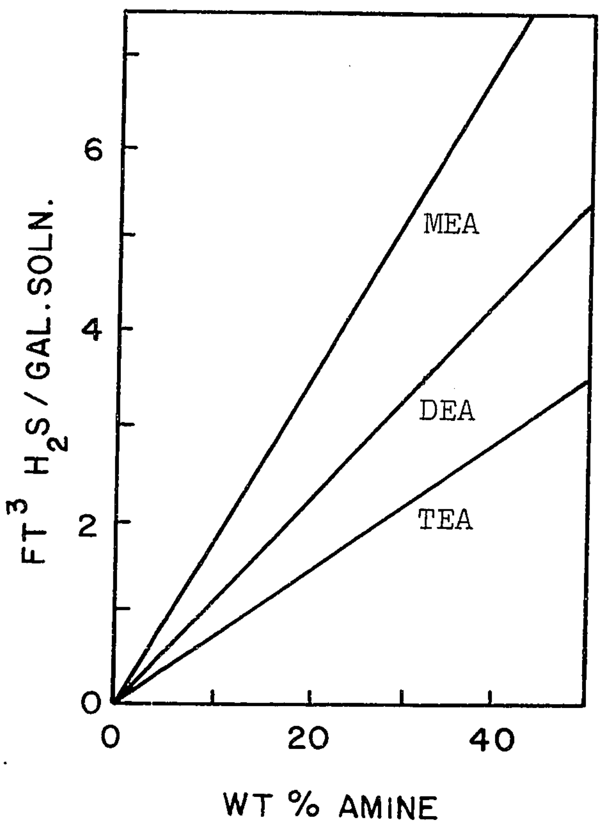


Figure 9. ACID GAS CAPACITY WITH VARYING CONCENTRATIONS OF AMINE SOLUTIONS.

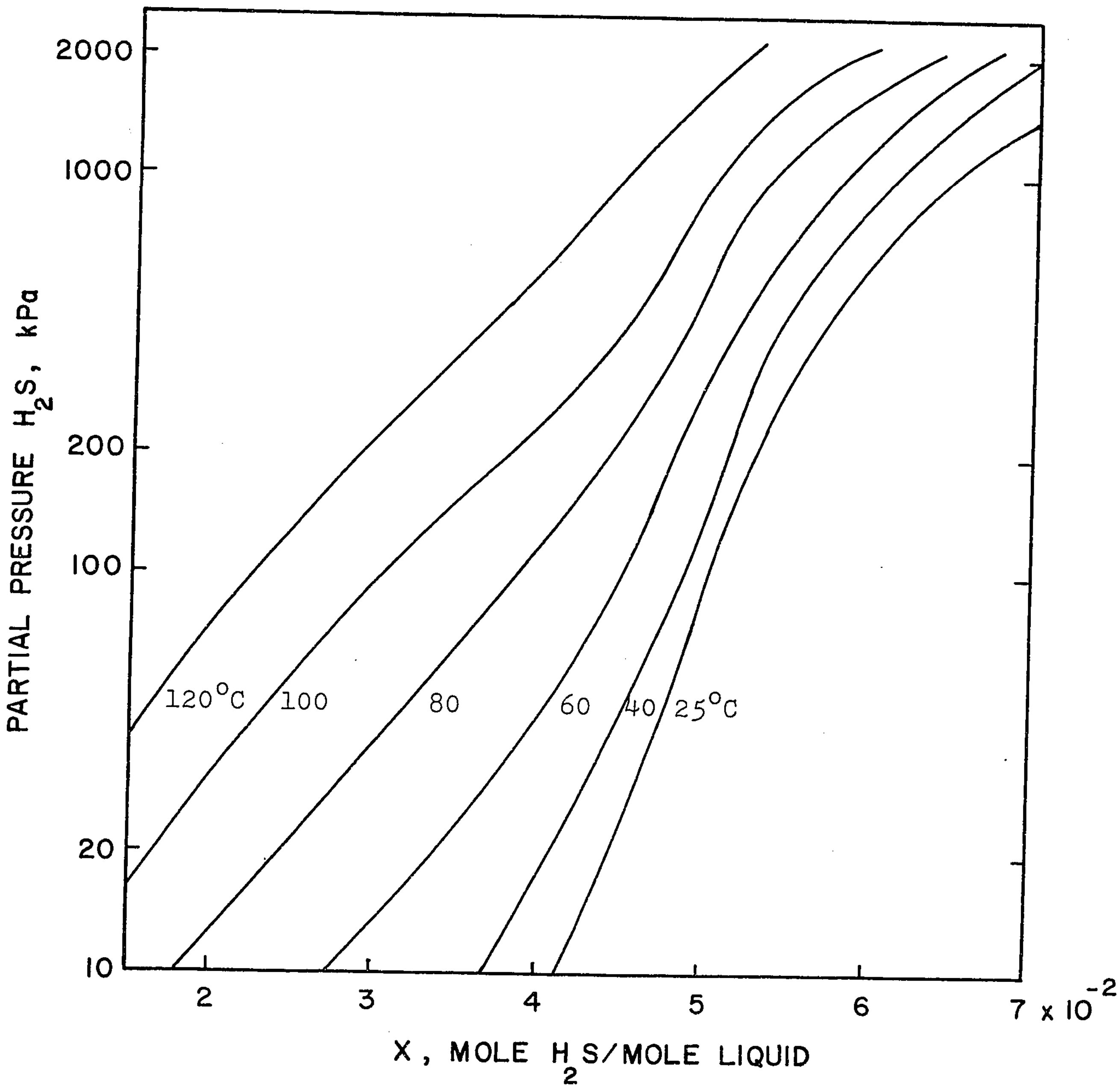


Figure 10. SOLUBILITY OF H_2S IN 2.5 N MEA SOLUTION.

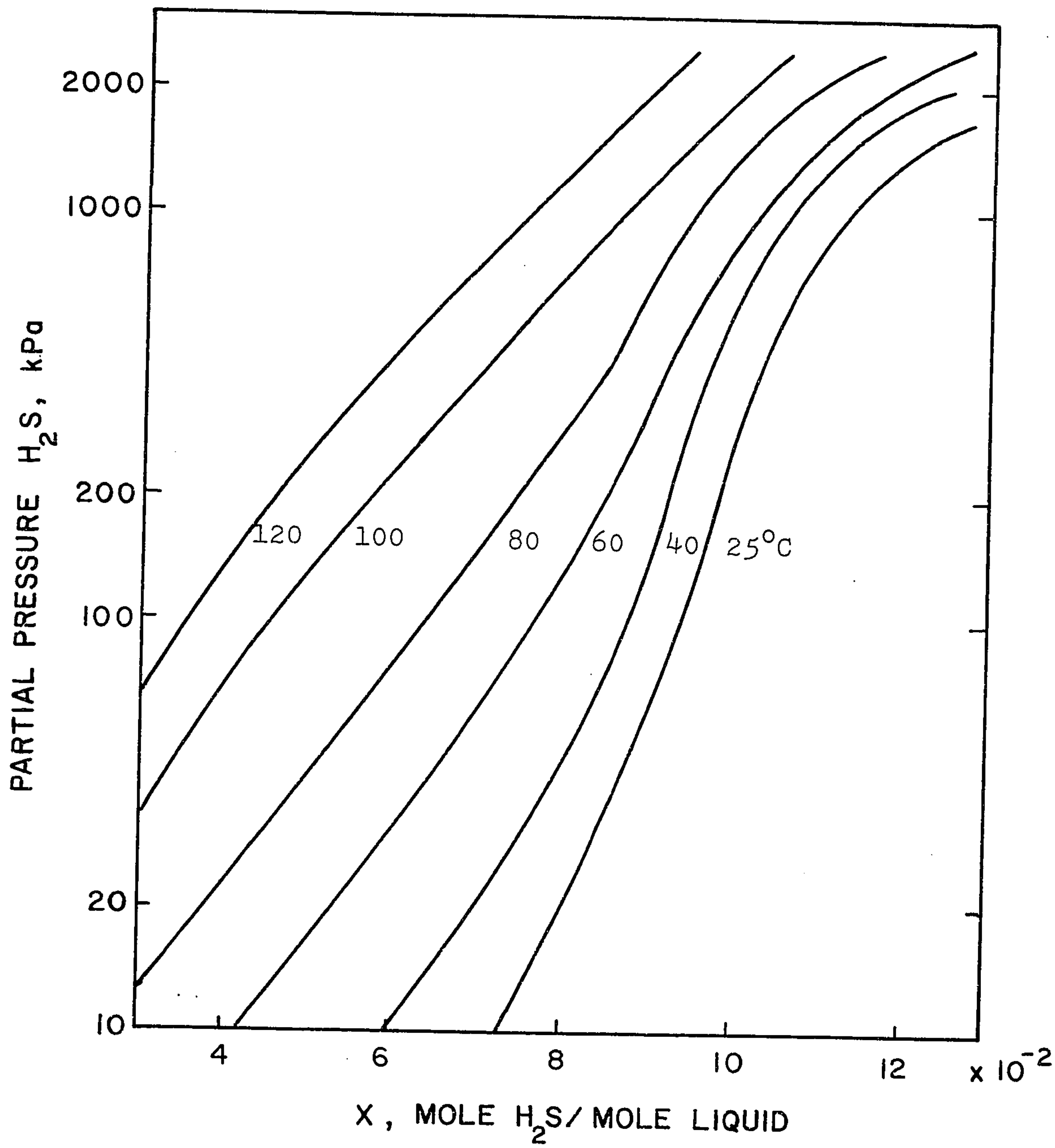


Figure 11. SOLUBILITY OF H_2S IN 5 N MEA SOLUTION.

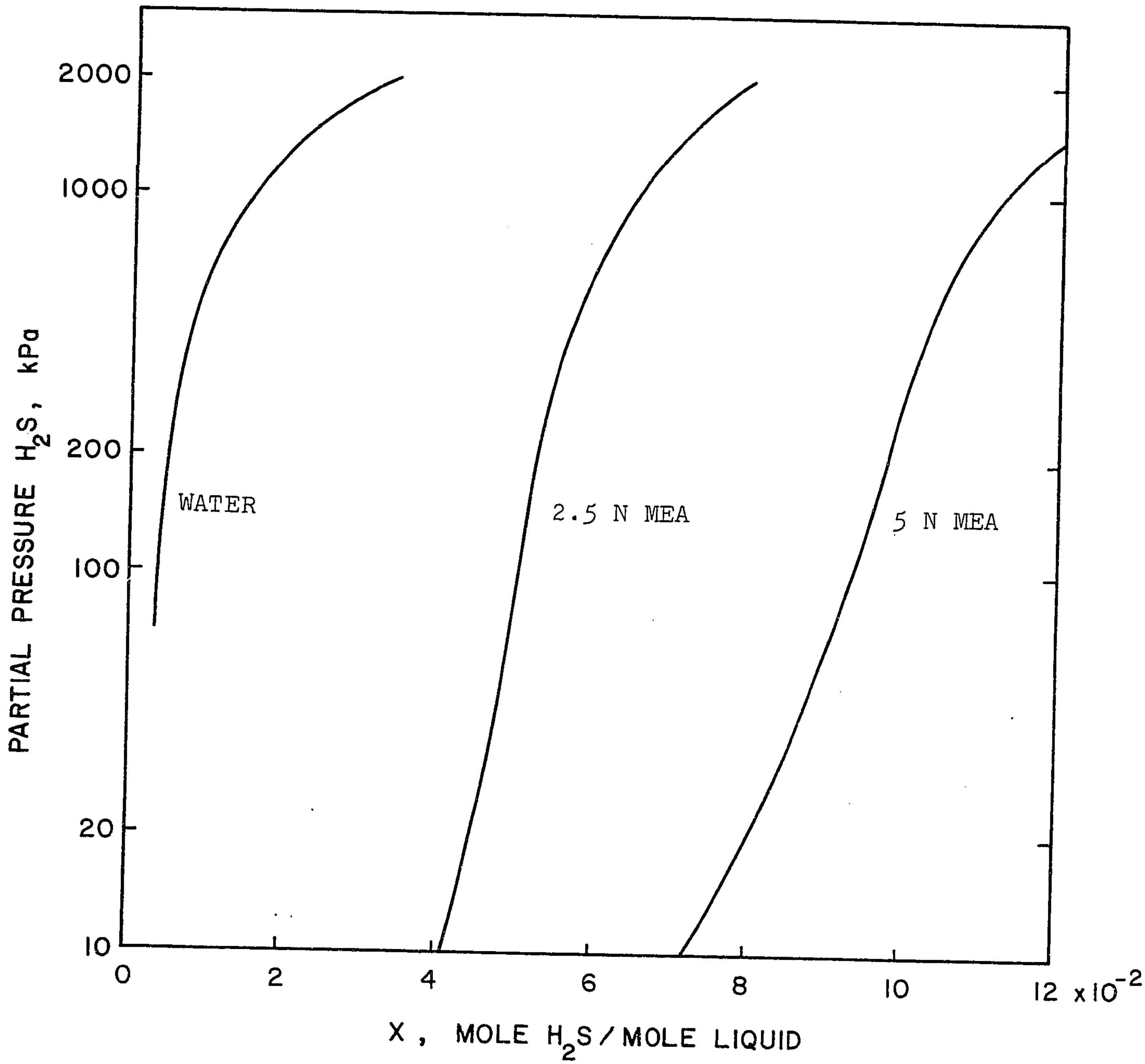


Figure 12. SOLUBILITY OF H_2S IN WATER AND MEA SOLUTIONS AT 25 ^{o}C.

Figure 13 shows the vapor-liquid composition and boiling point curve for aqueous MEA solutions (19). Table 4 compares the experimental vapor pressures of MEA with those values calculated from the Antoine equation (23):

$$\log P^{o} = A - \frac{B}{T + C} \qquad \ldots (24)$$

3. Effects of MEA on the overall separation factor:

The vapor pressure of MEA is small at the G.S. temperatures and pressure. It was assumed that the water vapor content in the gas phase of first-stage G.S. towers did not change at low MEA concentrations (less than 30 wt% in the liquid). Then the overall separation factor was evaluated using equations (19), (22), and (23), utilizing the fact that only the solubility, S, was significantly changed.

Figure 14 shows the effect of a variation in MEA concentration on the overall separation factor. It may be observed that the presence of MEA slightly reduces the value of β (up to 6% for 30 wt% MEA at 31 ^{o}C and 304 psia) but it has little effect on the maximum theoretical fractional recovery. Consider a pair of towers operating at 304 psia, with the hot and cold towers maintained at 130 ^{o}C and 31 ^{o}C respectively. For water as

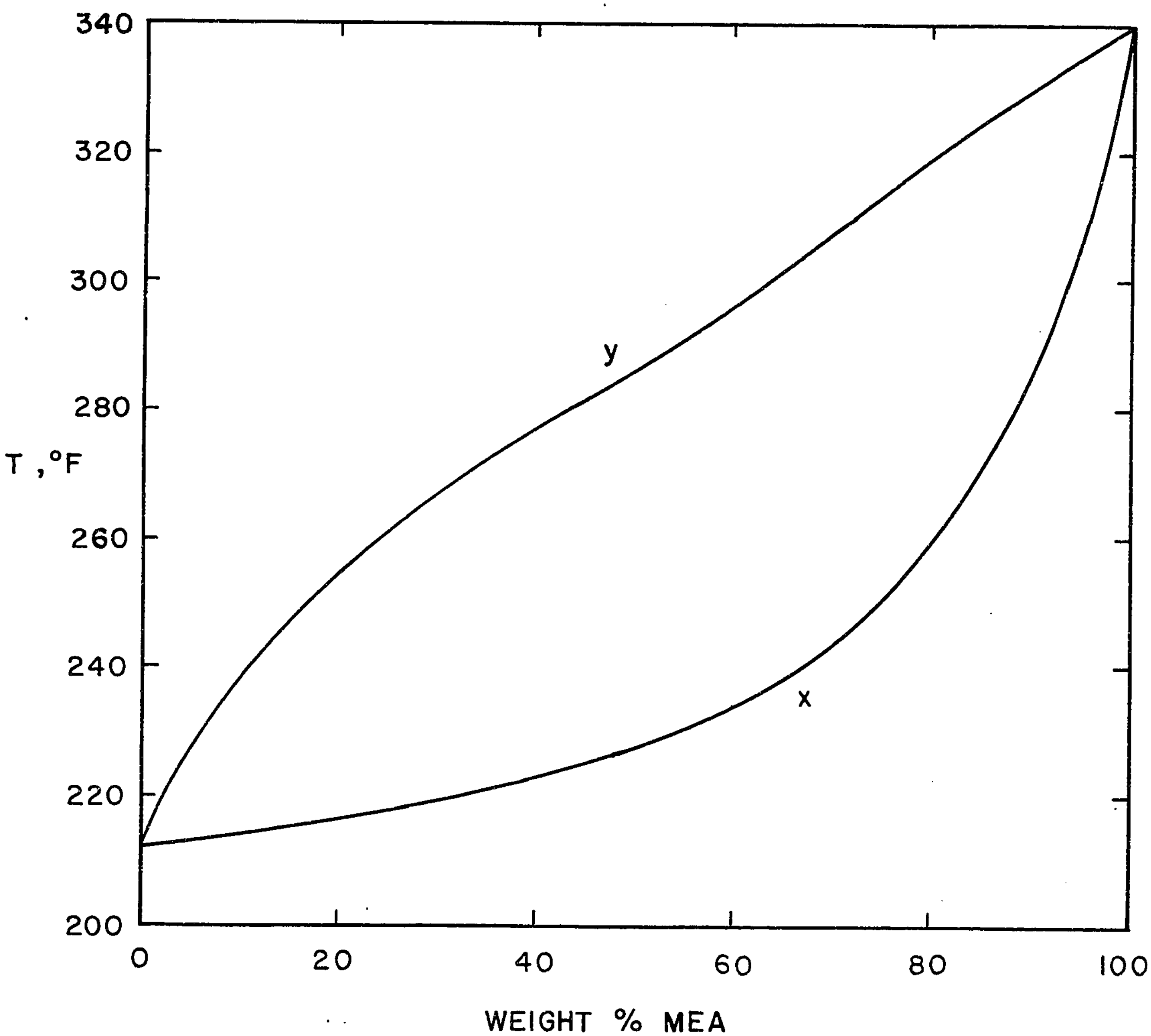


Figure 13. VAPOR-LIQUID COMPOSITION AND BOILING POINT CURVE FOR AQUEOUS-MEA SOLUTIONS.

Table 4. Vapor pressure of monoethanolamine.

Temperature ^{o}C	P^{o}_{exp} mm Hg	P^{o}_{cal} mm Hg
65.5	7.1	7.1
71.0	9.8	10.0
75.4	13.2	13.0
85.0	21.7	22.4
90.0	28.6	29.2
101.7	53.6	52.6
112.1	84.8	85.1
121.0	122.9	125.1
132.0	193.3	195.1
141.5	280.0	279.4
150.8	406.5	389.0
161.4	554.0	554.7
167.0	652.0	663.1
170.9	751.0	748.3

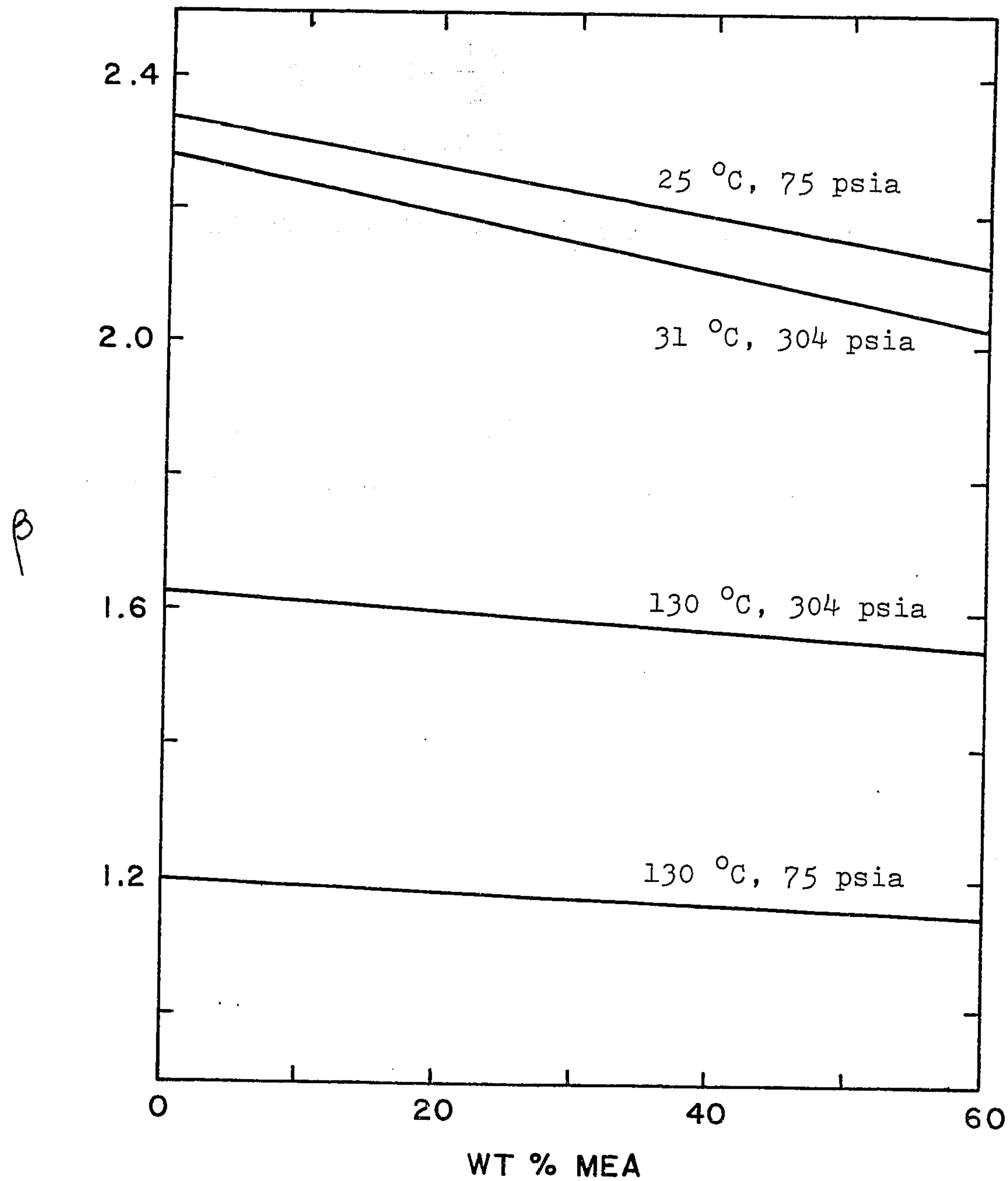


Figure 14. EFFECT OF MEA CONCENTRATION ON THE OVERALL SEPARATION FACTOR.

solvent the fractional recovery is:

$$F_o = 1 - \frac{\beta_h}{\beta_c}$$
$$= 28.7 \%$$

At 15 wt% MEA the fractional recovery is:

$$F_{15} = 27.7 \%$$

The actual fractional recovery based on data taken at the Savannah River plant (U.S.A.) is about 18 %.

APPARATUS AND PROCEDURE

The schematic diagrams of the experimental equipment for the heavy water concentration studies are shown in figures 15 and 16. The equipment consisted of two 316 SS columns of 1 in. I.D. and 36 in. in length. Each column was packed with $\frac{1}{4}$ in. glass raschig rings to a depth of about 31 in.. The H_2S gas was circulated upward through each column by means of a gas metering pump. Aqueous H_2S-saturated solution (stored at the bottom of each column) was circulated in a direction countercurrent to the gas flow by means of a duplex metering pump.

The hot column temperature was maintained at approximately 130 ^oC by means of a temperature controller using electrical heating tapes wound around the column. A small condenser was placed inside the top section of the hot column to condense the water vapor and hence kept it from escaping to the cold column with the gas stream. All parts of the hot column subjected to heat loss were insulated with asbestos cloth or asbestos cement.

The cold column temperature was maintained at 25 ^oC by means of a flow of temperature controlled water circulated through the column jacket. A hand screw-pump was provided for each column to feed the liquid into the absorption

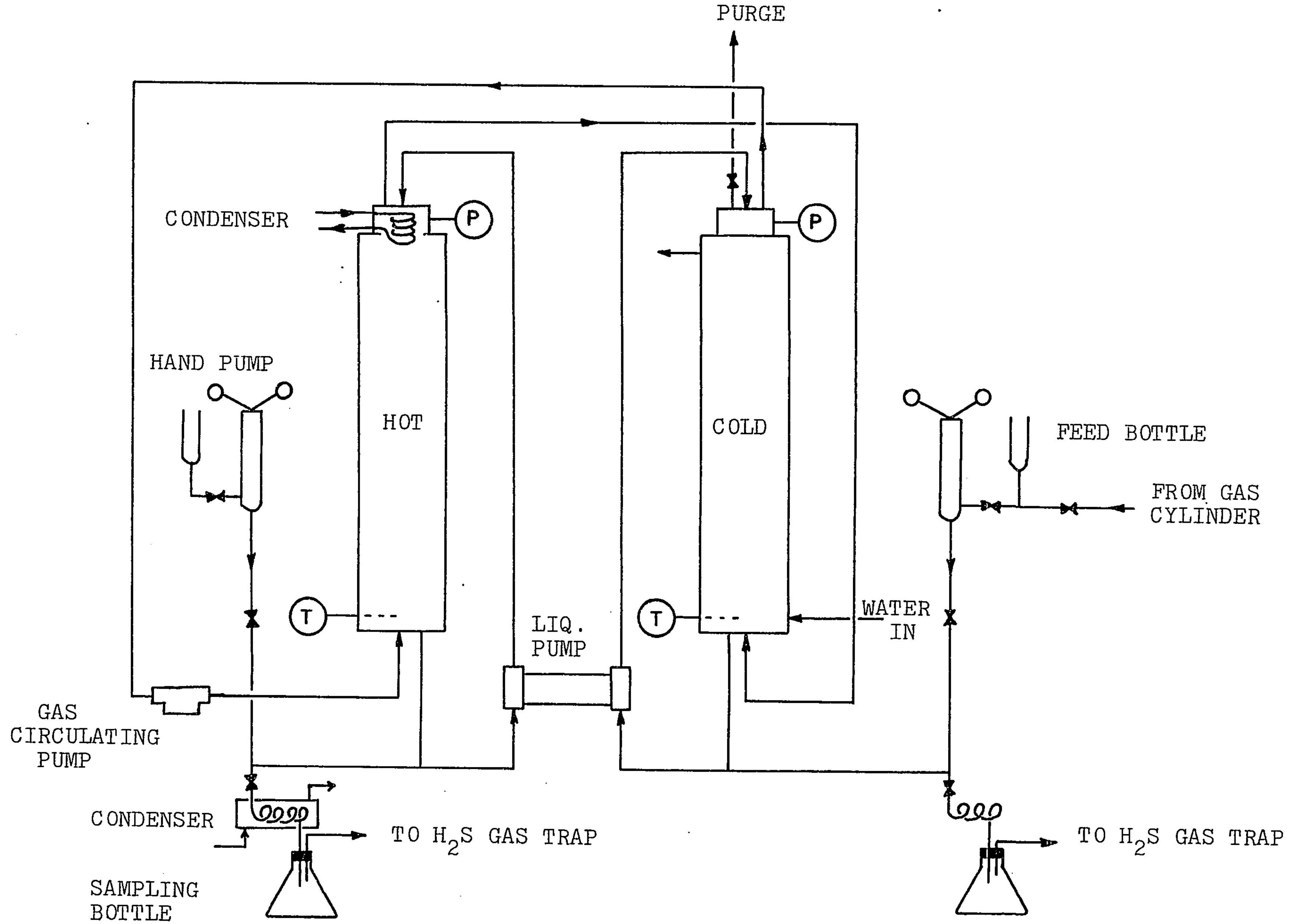


Figure 15. SCHEMATIC DIAGRAM OF EQUIPMENT

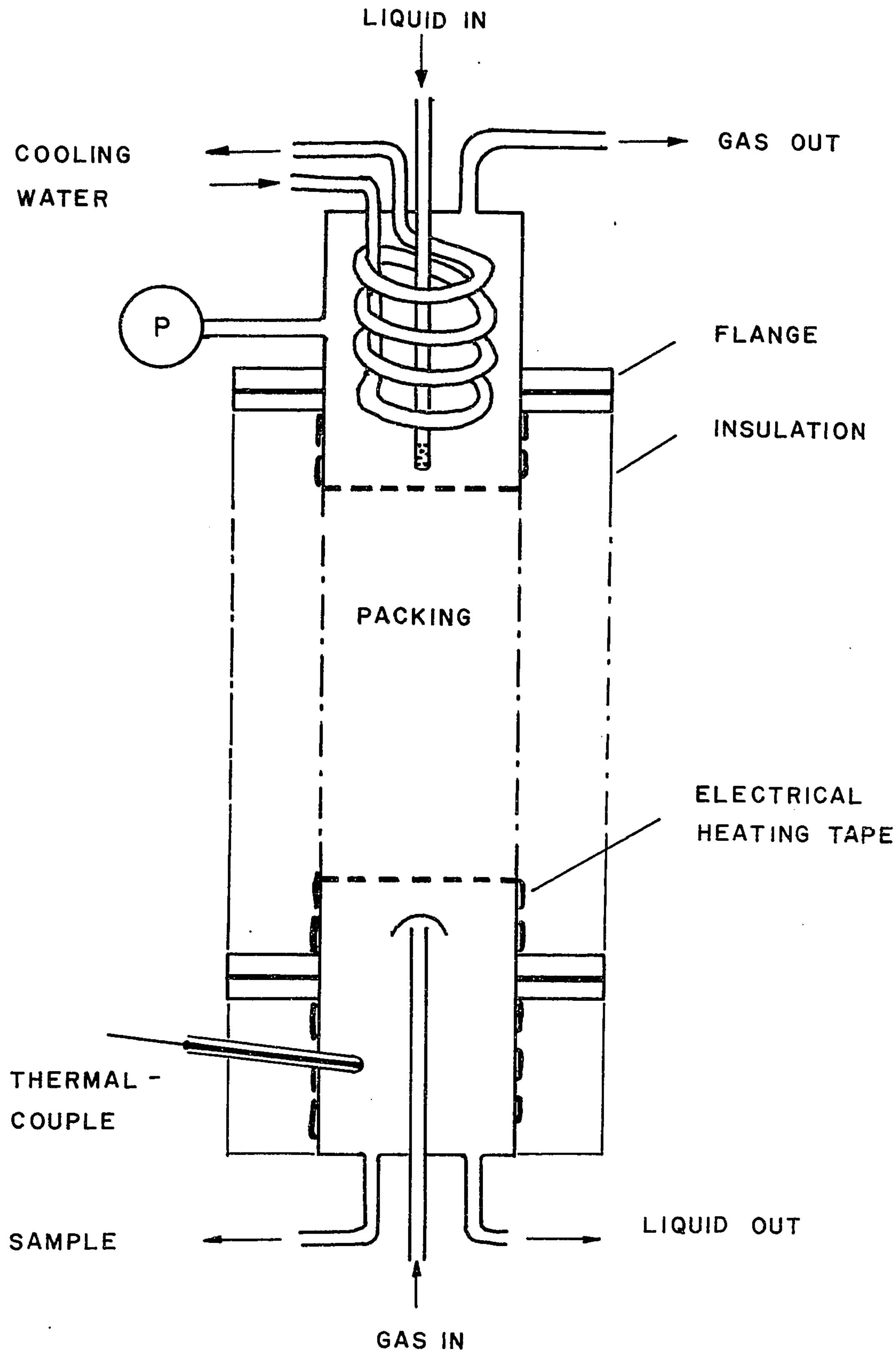


Figure 16. SCHEMATIC DIAGRAM OF THE HOT COLUMN

system while it was under pressure. All gas and liquid lines were of 1/8 in. stainless steel tubing. The whole equipment was mounted on a support rack and placed inside an enclosed fume hood for safety reasons.

Before each run, the columns were flushed many times with fresh D_2O solution having a concentration identical to the concentration of the solution to be charged into the system. Fresh H_2S was also charged into the system for every run. Each column was initially charged with 100 ml of D_2O solution of the same concentration. Both columns were heated up to the desired temperatures and charged with H_2S (99.6%) simultaneously to the desired pressure. Then the pumps were started. Each run was of six hours duration. Finally liquid samples were withdrawn at the bottom of each column for analysis. Any gas escaping from the system or solution while samples were taken was passed through a lead acetate solution for removal. The samples were degassed before analysis for D_2O content since the presence of H_2S would have caused bubble formation in the I.R. cells and hence erroneous analyses. In the case of samples containing MEA, it was necessary to distill the aqueous portion of the solution because of the effect of MEA on the D_2O absorption band. The distillation did not cause any detectable change in D_2O concentration. Figures 17 and 18 show the distillation and degassing apparatus.

The following were the operating conditions for all runs:

Pressure = 75 psia

Hot column temperature = 130 ^{o}C

Cold column temperature = 25 ^{o}C

Initial liquid charge to each column = 100 ml

Gas rate = 50 ml/min. at 25 ^{o}C and 75 psia

Liquid circulation rate for each column = 25 ml/min.

Initial concentrations of D_2O for aqueous solutions: 0.11 wt% and 0.22 wt%

Concentration of D_2O in aqueous-MEA solutions : 0.11 wt% for MEA concentrations of 0.1, 0.5, 1.0, 2.5, and 5 N.

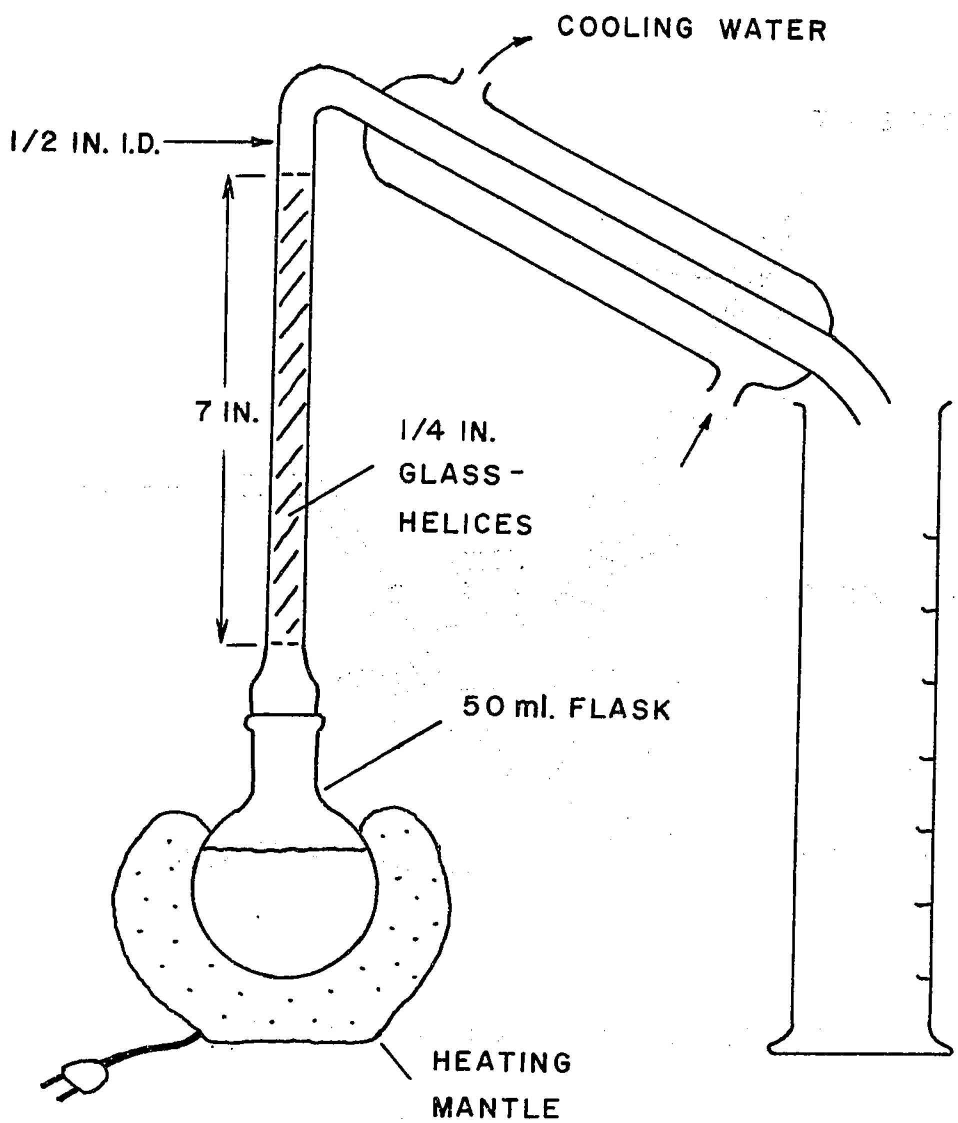


Figure 17. DISTILLATION APPARATUS

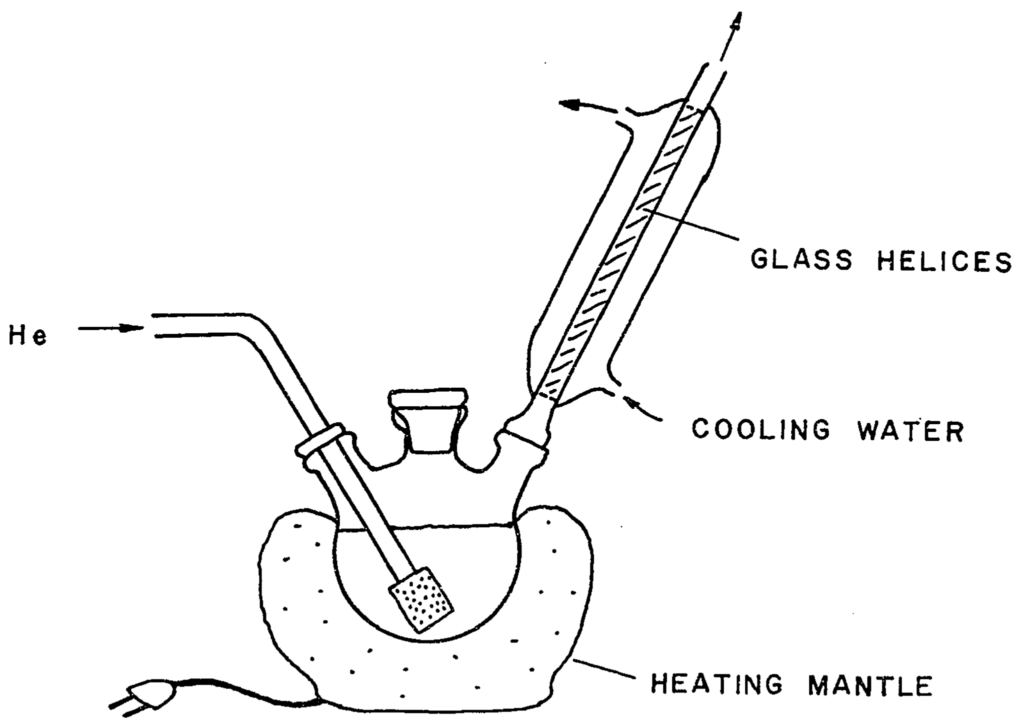


Figure 18. DEGASSING APPARATUS

PROPERTIES OF, AND SAFETY PRECAUTIONS IN HANDLING H_2S AND AQUEOUS SOLUTIONS

Hydrogen sulfide is often reconized by its very offensive odour of rotten eggs. Because the sense of smell is dulled with concentration above 100 ppm. exposure to such concentrations can be harmful. Hydrogen sulfide is a colourless flammable gas with a specific gravity of 1.18 in relation to air, therefore it may accumulate in depressions, or spread over floors to a source of ignition and flash back. It is highly flammable with an ignition temperature of 500 ^{o}F. The H_2S explosive range in air is from 4.3 to 46 volume percent.

Carbon steel vessels or lines containing H_2S will normally develop an interior coating of pyrophoric iron sulfide according to the following reaction:

$$Fe + H_2S \rightleftharpoons FeS + H_2$$

Carbon steel is corroded by H_2S in water but the FeS coating acts as a protective layer. Carbon steel is used in the G.S. process, only for equipment not subject to highly turbulent liquid flow, which prevents the formation of the FeS coating. In practice, carbon steel is satisfactory for tower shells, heat exchanger shells, tanks and most process piping. Stainless steel type 316 is most resistant, whereas type 304 is acceptable in most parts where high liquid velocities are unavoidable (as in control valves, through bubble-cap trays and heat exchanger tubes).

Hydrogen sulfide is a highly toxic gas which even at low concentrations (less than 10 ppm.) causes irritation of mucous membranes. At concentrations above 20 ppm. it attacks the central nervous system, causing headache, dizziness, and eventual respiratory paralysis. Death can occur at concentrations of about 400 ppm. or greater.

The sense of smell should not be relied upon to warn of the presence of hydrogen sulfide. A strip of white absorbent paper soaked with lead acetate solution was used as an H_2S detector. It initially turned brown then black when exposed to H_2S concentrations as low as 1 ppm. Lead acetate solution was also used to react with escaping H_2S gas. A 10% solution (10 g lead acetate added to 95 ml of water and 5 ml of acetic acid) was found to have a high capacity for H_2S. Figure 19 shows a typical H_2S indicator, which can be hung on the laboratory wall at a convenient location. The design was obtained from the Atomic Energy Laboratories at Chalk River, Ontario.

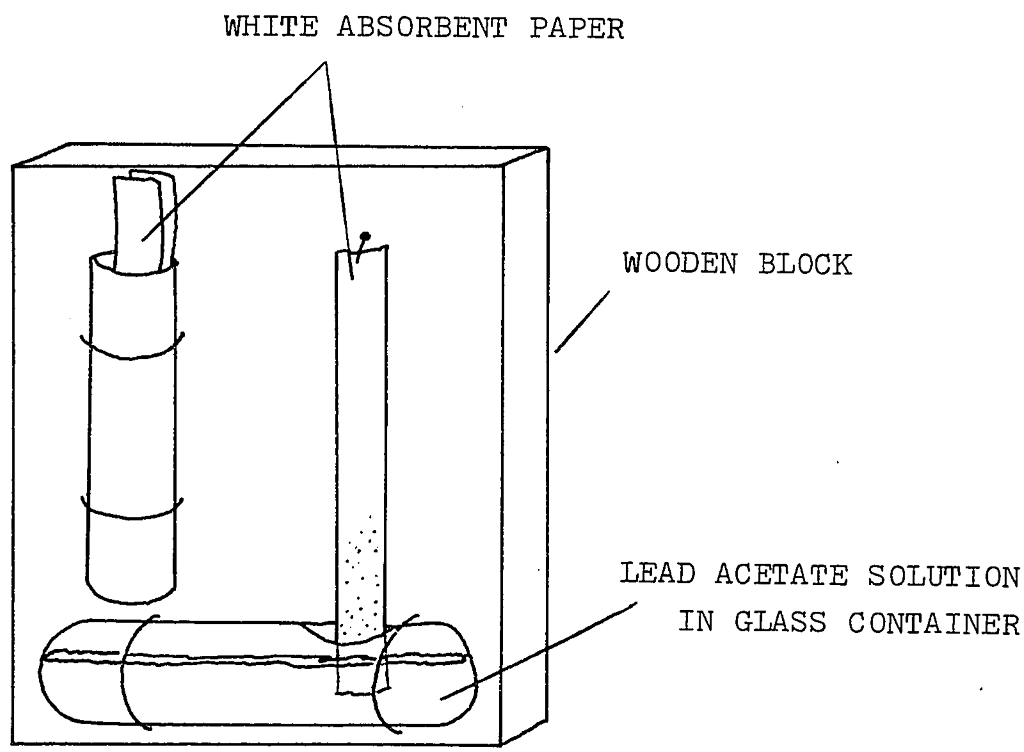
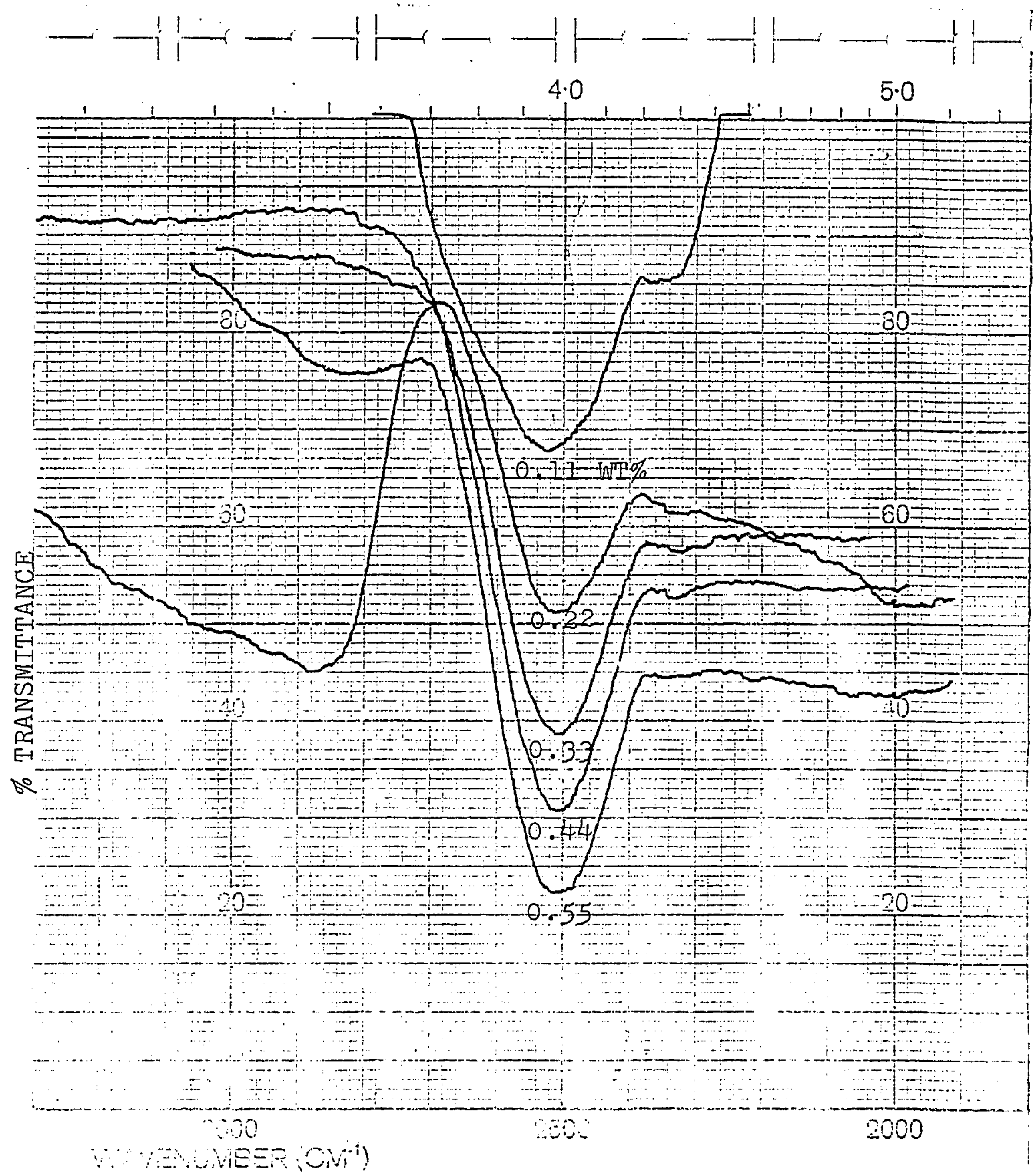


Figure 19. A TYPICAL H_2S INDICATOR

ANALYSIS OF AQUEOUS HEAVY WATER SOLUTIONS

The heavy water content of aqueous solutions can be determined by infra-red spectrometric methods. The double beam absorption methods were found suitable for analysis of samples with D_2O concentrations greater than 99.5% or less than 1% (24).

A Perkin-Elmer model 267 spectrophotometer equipped with a matching pair of cells with CaF_2 windows and 0.2 mm thick spacers was calibrated for the range 0.11 to 0.33 wt% D_2O. Standard solutions were prepared using 99.75 wt% D_2O. Distilled water was used in the reference cell. It was found that the I.R. absorption of the samples was extremely temperature sensitive (25). Therefore the instrument was allowed to warm up to its ultimate operating temperature and all the measurements were made at a cell temperature of 121 $^{\circ}F$. To prevent bubbles from forming in the cells, the samples were purged with helium and then preheated to about 121 $^{\circ}F$. The concentrations were determined from the peak heights of the absorption bands at the wave number 2500 cm^{-1}. Figures 20 and 21 show typical results.



CELL TEMPERATURE = 122 °F
ORIGIN %T = 90 AT
WAVENUMBER = 4000 CM^{-1}

SOLVENT DISTILLED WATER
CONCENTRATION 0.11 - 0.55 WT% D_2O
CELL PATH 0.2 mm
REFERENCE DISTILLED WATER

Figure 20. INFRA-RED SCAN

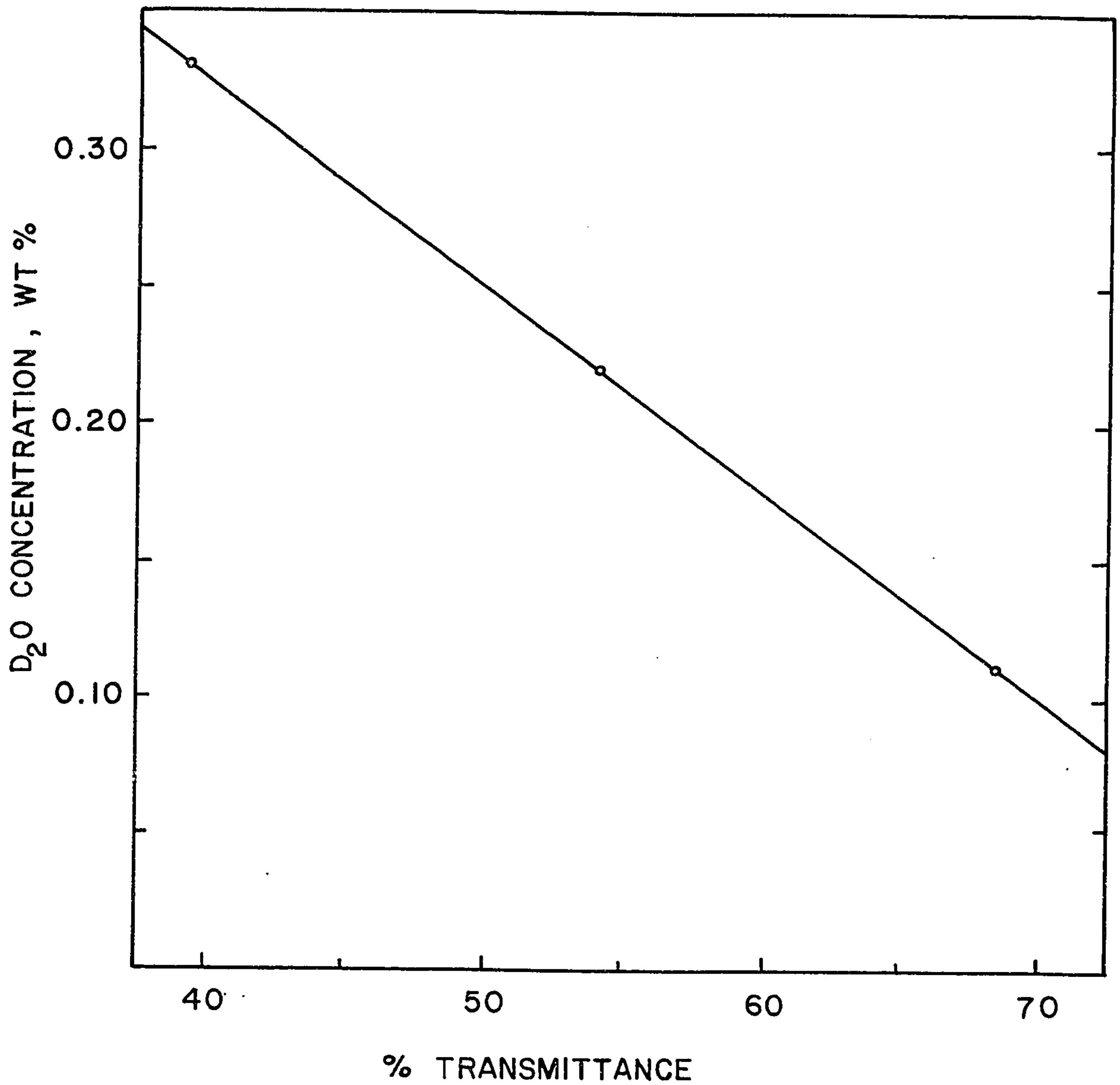


Figure 21. CALIBRATION OF THE INFRA-RED SPECTROPHOTOMETER FOR DILUTE HEAVY WATER SOLUTIONS

RESULTS AND DISCUSSIONS

For initial concentrations of 0.110 and 0.220 wt% D_2O in each of the columns, after 6 hours of circulation, a change in D_2O concentration was observed, particularly in the solutions in the hot column. The results are summarized in tables 5 and 6. It is noted that whereas a large (27%) decrease in concentration was observed in the hot column, no comparable increase in D_2O concentration in the cold column was observed. It became evident that some water had become transferred from the hot column to the cold column during the circulation, thus reducing the isotope concentration there. It was not possible to make a complete material balance for HDO because the volume and isotope content of the gas phase could not be determined. Nonetheless a consistent reduction in concentration of D_2O was observed for the solution in the hot column. The dilution of the liquid in the cold column was also verified by measuring the liquid volumes.

For each run, it was estimated that approximately 38% of the D_2O content in the hot column was removed. About 10% of this amount was transferred to the cold column, while the remainder stayed in the gas phase as HDS. The absorption system failed to actually increase the D_2O concentration in the cold column (although D_2O

Table 5. Results for the H_2O-H_2S system

Run No	Initial concn. wt%	Hot column		Cold column	
		Final concn. wt%	Reduction in concn., wt%	Final concn. wt%	Increase in concn., wt%
1	0.1104	0.080	27	0.110	
2	0.1104	0.080	27	0.110	
3	0.1104	0.085	26	0.095	NIL
4	0.2209	0.160	27	0.220	
5	0.2209	0.160	27	0.216	

Table 6. Results for the H_2O-MEA-H_2S system with initial D_2O concentration of 0.1104 wt%

Run No	MEA concn. wt%	Hot Column		Cold column	
		Final concn. wt%	Reduction in concn., wt%	Final concn. wt%	Increase in concn., wt%
6	0.1 N	0.080	27	0.110	
7	0.5 N	0.078	28	0.110	
8	1.0 N	0.082	26	0.108	NIL
9	2.5 N	0.080	27	0.106	
10	5.0 N	0.082	26	0.110	

was transferred to it) for two reasons. Firstly, an average of 15% of the liquid from the hot column was passed into the cold column along with the gas stream during the 6 hour period. This diluted the D_2O solution in the cold column. If the steam was to be condensed totally at the top of the hot column then the temperature at that section would have to be kept at approximately the same temperature as that of the cold column. This "cold spot" would have caused the reverse exchange reaction to occur at the top of the hot column and hence would have prevented any significant concentration change from occurring. In a continuous flow process, liquid from the upper parts of the cold tower is heated and fed back to the hot tower. Secondly, the large quantity of H_2S in the system, both gaseous as well as in solution, also reacted with some of the deuterium isotope, which was initially in the liquid.

It may be concluded from the results that the presence of MEA had little or no effect on the fractional recovery in these experiments. But, by introducing MEA into the absorption towers the solvent capacity for H_2S was increased while the effective water partial pressure was decreased. Hence the gas rate could be slightly increased which in turn increased the production rate.

On a McCabe-Thiele diagram, figure 22, it is shown that the slopes of the equilibrium lines for the G.S. process using MEA are greater than those without MEA. Hence the slopes of the operating lines are also increased. The significant is that for the same liquid feed rate the gas rate can be reduced, consequently slightly smaller tower diameters could be used for the same absorption rate, or both liquid and gas rates could be increased to obtain a higher production rate without flooding the towers. It is noted that the gas rate is the main factor which determines the flooding character of the absorption towers in the G.S. process. Figure 23 shows the estimation of the effect of MEA on the production rate based on data of Burgess (figure 8). The improvement of the G.S. process by using MEA is relatively small, especially when it is considered that one more stage must be added for the recovery of MEA.

The ability of providing a laboratory apparatus for the concentration of HDO has been a rewarding one in terms of experience. Future experiments may be more rewarding in terms of processing improvements.

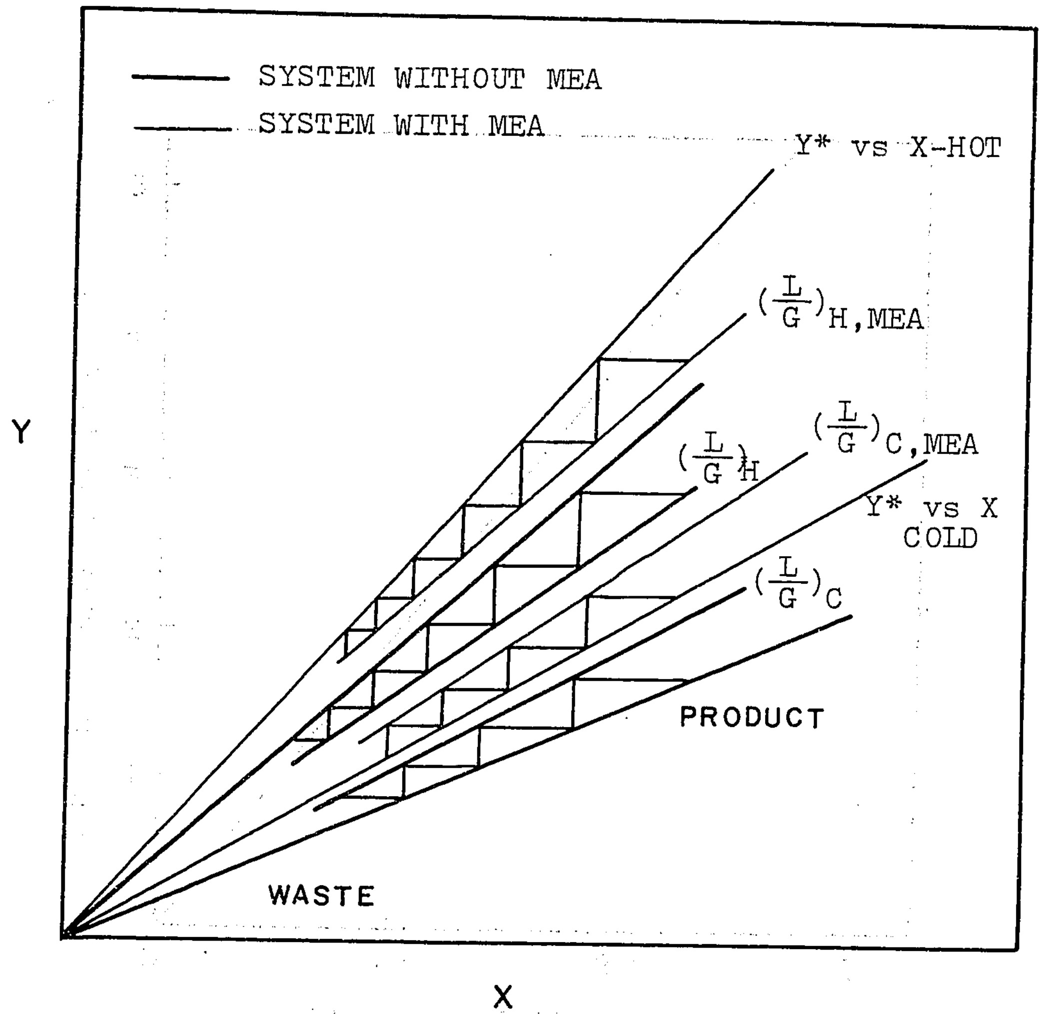


Figure 22. EFFECT OF MEA ON THE EQUILIBRIUM AND OPERATING LINES OF FIRST-STAGE G.S. TOWERS

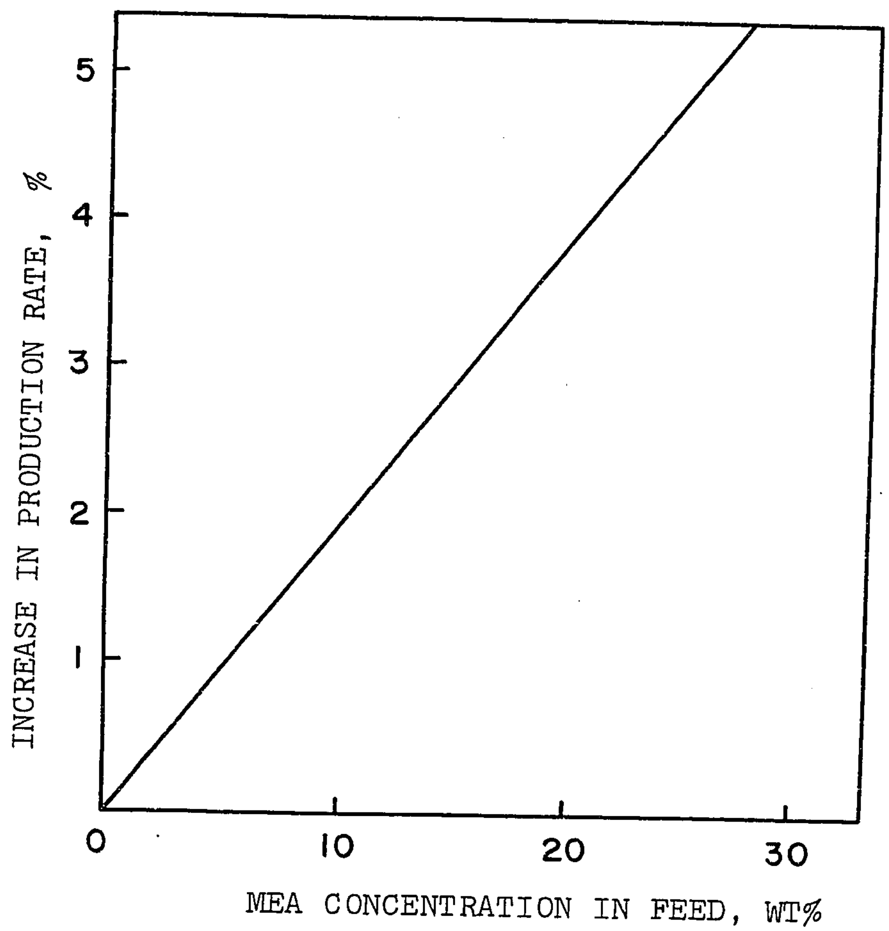


Figure 23. EFFECT OF MEA ON THE PRODUCTION RATE IN THE G.S. PROCESS

BIBLIOGRAPHY

(1) Haywood L.R., "Heavy water production", Nu. Eng. Int., 19, p.506, 1974.

(2) Galley M.R., Miller A.I., Atherley J.F. and Mohn M., "G.S. process physical properties", AECL-4255, 1973.

(3) Selak P.J. and Finke J., "Heavy water", Chem. Eng. Prog., 50, p.221, 1954.

(4) Rae H.K.,"A review of heavy water production processes", AECL-2503, 1965.

(5) White A.S., "Production of heavy water", Ind. Chem., p.672, Dec. 1958.

(6) Lefrançois B., Lerat J. and Roth E., "Study on the production of heavy water in France", paper 91, 3rd U.N. Int. Conf. on peaceful uses of A.E., Geneva, 1964.

(7) Barr F.T. and Drew W.P., "The future of cheap heavy water", Chem. Eng. Prog.,56, (3), p.49, 1960.

(8) Bebbington W.P. and Thayer V.R., "Production of heavy water", Chem. Eng. Prog., 55, (9), p.70, 1959.

(9) Elliott J.N., "Table of the thermodynamic properties of heavy water", AECL-1673, 1974.

(10) Selleck F.T., Carmichael L.T., and Sage B.H., "Phase behaviour in the Hydrogen sulfide-water system", Ind. Eng. Chem., 44, p.2219, 1952.

(11) Burgess M.P. and Germann R.P., "Physical properties of hydrogen sulfide-water mixtures", A.I.Ch.E. Jour., March 1969.

(12) Clarke E.C.W. and Glew D.N., "Aqueous nonelectrolyte solutions. Part VIII. Deuterium and hydrogen sulfides solubilities in Deuterium oxide and water", Can. J. Chem., 49, p.691, 1971.

(13) Wright R.H. and Maass O., "The solubility of hydrogen sulfide in water from the vapour pressures of the solutions", Can. J. Research, 5, p.442, 1931.

(14) Janik J., "Determination of density of liquids and their saturated vapors at pressure higher than 1 atm", Acta Physica Polonica, XXIII, p.487, 1963.

(15) West J.R., "Thermodynamic properties of hydrogen sulfide", Chem. Eng. Prog., 44, p.287, 1948.

(16) Reamer H.H., Sage B.H., and Lacey W.N., "Volumetric behaviour of hydrogen sulfide", Ind. Eng. Chem., 42, p.140,1950.

(17) Reid R.C. and Sherwood T.K., "The properties of gases and liquids", 2nd ed., Mc Graw-Hill, N.Y., 1966.

(18) Burgess M.P., "Mathematical model of Heavy water Extraction and Distillation", AIChE, 17, (3), p.529, 1971.

(19) Connors J.S., "Aqueous-amine acid-removal process needn't be corrosive", Oil and Gas J., p.100, Mar.3, 1958.

(20) Lee J.I., Otto F.D., and Mather A.E., "Equilibrium in hydrogen sulfide-monoethanolamine-water system", J. Chem. Eng. Data, 21, (2), p.207, 1976.

(21) Riegger E., Tartar H.V., and Lingalfelter E.C., "Equilibria between hydrogen sulfide and aqueous solutions of monoethanolamine at 25°, 45° and 60°", J.Am.Chem.Soc., 66, p.2024, 1944.

(22) Atwood K., Arnold M.R., and Kindrick R.C., Ind. Eng. Chem., 49, p.1439, 1957.

(23) Boublik T., Fried V., and Hala E., "The vapour pressure of pure substances", Elsevier Scientific Pub. Co., N.Y., p.102, 1973.

(24) Steven W.H. and Thurston W., "The determination of the D_2O content of heavy water by infra-red spectrometry", AECL-295, 1954.

(25) Bisset D., "Solution properties of heavy water", M.A.Sc. thesis, Dept. of Chem. Eng., Univ. of Ottawa, Ottawa, 1976.

APPENDIX

Table 7. Calibration of the infra-red spectrophotometer

D_2O concentration wt%	% transmittance at wavenumber 2500 cm^{-1}		
0.1104	68.5	68.5	68.4
0.2209	54.0	53.9	54.0
0.3314	39.5	39.6	39.5

Table 8. Tabulation of data

Run No.	% transmittance (hot column liq.)		% transmittance (cold column liq.)		Volume of water passed to cold col., ml
1	72.5	73.0	68.5	68.5	16
2	72.0	72.5	68.5	69.0	12
3	71.5	71.0	69.5	70.0	17
4	62.0	62.0	54.0	54.5	13
5	62.5	62.0	54.5	54.5	14
6	72.0	72.5	68.5	68.5	12
7	72.5	72.5	68.5	68.0	14
8	72.0	71.5	68.5	69.0	15
9	72.5	72.5	69.0	69.0	18
10	71.5	72.0	68.5	68.5	16

Table 9. Smoothed data for solubility of H_2S in aqueous-MEA solutions (20).

MEA concn.	T, ^oC / P_{H_2S}, kPa	X, mole H_2S/mole(H_2O+MEA) 25	40	60	80	100	120
2.5 N	31.6	0.0463	0.0435	0.0369	0.0283	0.0201	0.0135
	100	0.0498	0.0485	0.0446	0.0387	0.0304	0.0227
	316	0.0548	0.0531	0.0497	0.0468	0.0429	0.0339
	1000	0.06513	0.0617	0.0582	0.0536	0.0497	0.0446
	2000	0.0794	0.0709	0.0670	0.0629	0.0583	0.0514
5.0 N	31.6	0.0843	0.0756	0.0596	0.0433	0.0287	0.0206
	100	0.0929	0.0872	0.0769	0.0628	0.0457	0.0351
	316	0.1006	0.0942	0.0889	0.0813	0.0650	0.0533
	1000	0.1121	0.1053	0.1008	0.0938	0.0859	0.0751
	2000	0.1407	0.1232	0.1159	0.1076	0.0995	0.0897
	2500	. . .	. . .	0.1267	0.1164	0.1056	0.0936

Table 10. Effect of MEA on the overall separation factor,

T, °K	P, psia	MEA concn. mole%	β
403	75	0	1.1994
403	75	15.24	1.1862
403	75	30.48	1.1774
403	304	0	1.6329
403	304	15.24	1.6053
403	304	30.48	1.5823
304	304	0	2.2798
304	304	15.24	2.2274
304	304	30.48	2.1484
298	75	0	2.3411
298	75	15.24	2.2817
298	75	30.48	2.2313

```
$JOB   ACCT-NUM,NGUYEN 0
C...
C...  CALCULATION OF THE OVERALL DEUTERIUM DISTRIBUTION CONSTANT, BETA
C...  FOR THE GIRDLER SULFIDE PROCESS
C...
C...  NOMENCLATURE
C       P, PRESSURE IN PSIA
C       T, TEMPERATURE IN DEG. KELVIN
C       SOL, MOLE FRACTION OF THE DISSOLVED H2S
C       HUMID, H2O MOLE FRACTION IN VAPOR
C       ALPHA, RELATIVE VOLATILITY OF H2O AND HDO
C       XK, EQUILIBRIUM CONSTANT
C       BETA, OVERALL DISTRIBUTION CONSTANT
C DATA FOR THE SOLUBILITY CALCULATION, T LESS THAN 100 DEG. C
        READ,A,B,C,D,E,F,G
C DATA FOR SOLUBILITY CALCULATION, T GREATER THAN 100 DEG. C
        READ,AA,BB,CC,DD,EE,FF,GG
C DATA FOR HUMIDITY CALCULATION
         READ,HA,HB,HC,HD,HE,HF,HG,HH,HJ,HK
        READ,T
        TT=T
C CALCULATION OF SOL AND HUMID
        PRINT 2
  2       FORMAT(//' ','TEMP',6X,'PRESS',7X,'SOL',6X,'HUMIDITY',5X,
       1'ALPHA',9X,'K',9X,'BETA',//)
 11     P=71.
        DO 5 I=1,10
        IF(T.GT.373.) GO TO 6
        SS=A+(B*P)-(C*P**2)
        S1=(D*P**3)-(E*T)+(F*T**2)+(G*T**3)
        S2=SS+S1
        SOL=EXP(S2)
        GO TO 7
  6     S3=-AA+(BB*P)-(CC*P**2)+(DD*T)
        S4=-(EE*T**2)-(FF*P*T)+(GG*P**2*T**2)
        SOL=S3+S4
  7     W=ALOG(P)
        H1=-HA-(HB*W)+(HC*W**2)-(HD*W**3)+(HE*T)+(HG*T**3)
        H2=-(HF*T**2)+(HH*T*W)-(HJ*T**2*W**2)+(HK*T**3*W**3)
        H3=H1+H2
        HUMID=EXP(H3)
C CALCULATION OF ALPHA AND XK
        ALPHA=1.1596*EXP(-65.43/T)
        XK=1.01*EXP(233./T)
C CALCULATION OF BETA
        X=SOL/(1.-SOL)
        Y=HUMID/(1.-HUMID)
        BETA=(1.+Y)*(X+XK)/(ALPHA*(1.+X)*(1.+Y*XK))
        PRINT 22,T,P,SOL,HUMID,ALPHA,XK,BETA
 22     FORMAT(/' ',F6.2,3X,F6.2,5F12.6)
        P=P+2.
  5      CONTINUE
        T=T+2.
        T1=T-TT
        IF(ABS(T1).GT.10.) GOTO 9
        GO TO 11
  9     STOP
        END
$ENTRY
```

TEMP	PRESS	SOL	HUMIDITY	ALPHA	K	BETA
296.00	71.00	0.009048	0.006039	0.929627	2.219124	2.357888
296.00	73.00	0.009206	0.005890	0.929627	2.219124	2.358105
296.00	75.00	0.009365	0.005750	0.929627	2.219124	2.358297
296.00	77.00	0.009525	0.005619	0.929627	2.219124	2.358466
296.00	79.00	0.009687	0.005494	0.929627	2.219124	2.358610
296.00	81.00	0.009851	0.005376	0.929627	2.219124	2.358735
296.00	83.00	0.010016	0.005265	0.929627	2.219124	2.358837
296.00	85.00	0.010182	0.005159	0.929627	2.219124	2.358923
296.00	87.00	0.010350	0.005058	0.929627	2.219124	2.358992
296.00	89.00	0.010519	0.004962	0.929627	2.219124	2.359046
298.00	71.00	0.008704	0.006761	0.931007	2.207431	2.340618
298.00	73.00	0.008856	0.006594	0.931007	2.207431	2.340892
298.00	75.00	0.009009	0.006437	0.931007	2.207431	2.341135
298.00	77.00	0.009163	0.006289	0.931007	2.207431	2.341350
298.00	79.00	0.009319	0.006149	0.931007	2.207431	2.341546
298.00	81.00	0.009477	0.006016	0.931007	2.207431	2.341715
298.00	83.00	0.009635	0.005891	0.931007	2.207431	2.341862
298.00	85.00	0.009795	0.005772	0.931007	2.207431	2.341991
298.00	87.00	0.009957	0.005658	0.931007	2.207431	2.342099
298.00	89.00	0.010120	0.005551	0.931007	2.207431	2.342192
300.00	71.00	0.008379	0.007562	0.932371	2.195954	2.323478
300.00	73.00	0.008525	0.007374	0.932371	2.195954	2.323807
300.00	75.00	0.008672	0.007198	0.932371	2.195954	2.324107
300.00	77.00	0.008821	0.007031	0.932371	2.195954	2.324377
300.00	79.00	0.008971	0.006874	0.932371	2.195954	2.324619
300.00	81.00	0.009122	0.006725	0.932371	2.195954	2.324837
300.00	83.00	0.009275	0.006584	0.932371	2.195954	2.325030

300.00	85.00	0.009429	0.006451	0.932371	2.195954	2.325205
300.00	87.00	0.009584	0.006323	0.932371	2.195954	2.325357
300.00	89.00	0.009741	0.006202	0.932371	2.195954	2.325494
302.00	71.00	0.008070	0.008449	0.933719	2.184689	2.306446
302.00	73.00	0.008211	0.008239	0.933719	2.184689	2.306840
302.00	75.00	0.008353	0.008041	0.933719	2.184689	2.307195
302.00	77.00	0.008496	0.007854	0.933719	2.184689	2.307523
302.00	79.00	0.008640	0.007677	0.933719	2.184689	2.307817
302.00	81.00	0.008786	0.007510	0.933719	2.184689	2.308086
302.00	83.00	0.008933	0.007352	0.933719	2.184689	2.308331
302.00	85.00	0.009082	0.007202	0.933719	2.184689	2.308551
302.00	87.00	0.009231	0.007059	0.933719	2.184689	2.308750
302.00	89.00	0.009382	0.006923	0.933719	2.184689	2.308930
304.00	71.00	0.007778	0.009431	0.935050	2.173627	2.289507
304.00	73.00	0.007914	0.009195	0.935050	2.173627	2.289964
304.00	75.00	0.008050	0.008973	0.935050	2.173627	2.290384
304.00	77.00	0.008188	0.008764	0.935050	2.173627	2.290771
304.00	79.00	0.008328	0.008566	0.935050	2.173627	2.291122
304.00	81.00	0.008468	0.008379	0.935050	2.173627	2.291446
304.00	83.00	0.008610	0.008201	0.935050	2.173627	2.291744
304.00	85.00	0.008753	0.008033	0.935050	2.173627	2.292016
304.00	87.00	0.008897	0.007873	0.935050	2.173627	2.292263
304.00	89.00	0.009043	0.007720	0.935050	2.173627	2.292489
306.00	71.00	0.007501	0.010517	0.936367	2.162766	2.272636
306.00	73.00	0.007632	0.010253	0.936367	2.162766	2.273166
306.00	75.00	0.007764	0.010004	0.936367	2.162766	2.273653
306.00	77.00	0.007897	0.009770	0.936367	2.162766	2.274104
306.00	79.00	0.008031	0.009548	0.936367	2.162766	2.274520
306.00	81.00	0.008167	0.009338	0.936367	2.162766	2.274903
306.00	83.00	0.008303	0.009139	0.936367	2.162766	2.275253

TEMP	PRESS	SOL	HUMIDITY	ALPHA	K	BETA
401.00	71.00	0.001436	0.652328	0.985021	1.805789	1.200856
401.00	73.00	0.001516	0.630468	0.985021	1.805789	1.214840
401.00	75.00	0.001595	0.609937	0.985021	1.805789	1.228271
401.00	77.00	0.001675	0.590626	0.985021	1.805789	1.241177
401.00	79.00	0.001754	0.572442	0.985021	1.805789	1.253578
401.00	81.00	0.001834	0.555300	0.985021	1.805789	1.265496
401.00	83.00	0.001913	0.539114	0.985021	1.805789	1.276958
401.00	85.00	0.001992	0.523816	0.985021	1.805789	1.287981
401.00	87.00	0.002071	0.509299	0.985021	1.805789	1.298617
401.00	89.00	0.002150	0.495559	0.985021	1.805789	1.308846
403.00	71.00	0.001361	0.697250	0.985820	1.800590	1.171462
403.00	73.00	0.001439	0.673721	0.985820	1.800590	1.185756
403.00	75.00	0.001518	0.651649	0.985820	1.800590	1.199483
403.00	77.00	0.001596	0.630868	0.985820	1.800590	1.212700
403.00	79.00	0.001675	0.611317	0.985820	1.800590	1.225401
403.00	81.00	0.001753	0.592902	0.985820	1.800590	1.237610
403.00	83.00	0.001832	0.575514	0.985820	1.800590	1.249360
403.00	85.00	0.001910	0.559070	0.985820	1.800590	1.260678
403.00	87.00	0.001989	0.543482	0.985820	1.800590	1.271597
403.00	89.00	0.002067	0.528712	0.985820	1.800590	1.282117
405.00	71.00	0.001281	0.744689	0.986610	1.795455	1.142192
405.00	73.00	0.001359	0.719407	0.986610	1.795455	1.156762
405.00	75.00	0.001437	0.695687	0.986610	1.795455	1.170774
405.00	77.00	0.001515	0.673361	0.986610	1.795455	1.184272
405.00	79.00	0.001592	0.652365	0.986610	1.795455	1.197252
405.00	81.00	0.001670	0.632577	0.986610	1.795455	1.209747
405.00	83.00	0.001747	0.613900	0.986610	1.795455	1.221781

405.00	85.00	0.001825	0.596237	0.986610	1.795455	1.233382
405.00	87.00	0.001902	0.579511	0.986610	1.795455	1.244572
405.00	89.00	0.001980	0.563662	0.986610	1.795455	1.255363
407.00	71.00	0.001199	0.794729	0.987394	1.790387	1.113099
407.00	73.00	0.001275	0.767583	0.987394	1.790387	1.127925
407.00	75.00	0.001352	0.742111	0.987394	1.790387	1.142200
407.00	77.00	0.001429	0.718146	0.987394	1.790387	1.155962
407.00	79.00	0.001506	0.695615	0.987394	1.790387	1.169205
407.00	81.00	0.001582	0.674379	0.987394	1.790387	1.181967
407.00	83.00	0.001659	0.654335	0.987394	1.790387	1.194268
407.00	85.00	0.001736	0.635386	0.987394	1.790387	1.206134
407.00	87.00	0.001812	0.617443	0.987394	1.790387	1.217589
407.00	89.00	0.001889	0.600448	0.987394	1.790387	1.228638
409.00	71.00	0.001112	0.847535	0.988170	1.785382	1.084191
409.00	73.00	0.001188	0.818384	0.988170	1.785382	1.099265
409.00	75.00	0.001264	0.791051	0.988170	1.785382	1.113783
409.00	77.00	0.001340	0.765355	0.988170	1.785382	1.127785
409.00	79.00	0.001416	0.741172	0.988170	1.785382	1.141285
409.00	81.00	0.001491	0.718410	0.988170	1.785382	1.154289
409.00	83.00	0.001567	0.696923	0.988170	1.785382	1.166840
409.00	85.00	0.001643	0.676610	0.988170	1.785382	1.178956
409.00	87.00	0.001718	0.657383	0.988170	1.785382	1.190657
409.00	89.00	0.001794	0.639164	0.988170	1.785382	1.201960
411.00	71.00	0.001022	0.903127	0.988940	1.780438	1.055553
411.00	73.00	0.001097	0.871875	0.988940	1.780438	1.070839
411.00	75.00	0.001172	0.842568	0.988940	1.780438	1.085579
411.00	77.00	0.001247	0.815037	0.988940	1.780438	1.099799
411.00	79.00	0.001322	0.789114	0.988940	1.780438	1.113533
411.00	81.00	0.001397	0.764722	0.988940	1.780438	1.126771
411.00	83.00	0.001472	0.741707	0.988940	1.780438	1.139552

```
$JOB   ACCT-NUM,NGUYEN Q
C
C... CALCULATION OF THE COMPRESSIBILTTY FACTOR, Z FOR DRY H2S
C
C... NOMENCLATURE
C.
C... T, TEMPERATURE- DEG. KELVIN
C... P, PRESSURE- ATM.
C... B'S, VIRIAL COEFFICTENTS
C
      READ, B0,B1,B2,B3,B4,B5,B6,B7,B8
      READ ,B9,B10,B11,B12,B13,B14,B15,B16
      READ,T
      PRINT 25
      DO 5 I=1,3
      PRINT 15
      P=4.9
      DO 10 J=1,10
      W=B0+(B1/T)+(B2/T**2)+(B3/T**3)+(B4/T**4)
      W1=(B5*P/T)+(B6*P/T**2)+(B7*P/T**3)+(B8*P/T**4)
      W2=(B9*P**2/T)+(B10*P**2/T**2)+(B11*P**2/T**3)+(B12*P**2/T**4)
      W3=(B13*P**3/T)+(B14*P**3/T**2)+(B15*P**3/T**3)+(B16*P**3/T**4)
      Z=W+W1+W2+W3
      PRINT 20,T,P,Z
      P=P+0.1
10     CONTINUE
      T=T+2.0
5     CONTINUE
      PRINT 30
15     FORMAT(//' ')
20     FORMAT(/' ',3F12.6)
25     FORMAT(//' ',' TEMPERATURE',3X,' PRESSURE', 7X,'Z ',//)
30    FORMAT('1')
      STOP
      END

$ENTRY
```

TEMPERATURE	PRESSURE	Z
298.000000	4.900000	0.958510
298.000000	4.999999	0.957642
298.000000	5.099998	0.956773
298.000000	5.199998	0.955903
298.000000	5.299997	0.955033
298.000000	5.399997	0.954161
298.000000	5.499996	0.953289

298.000000	5.599996	0.952415
298.000000	5.699995	0.951541
298.000000	5.799994	0.950665
300.000000	4.900000	0.959535
300.000000	4.999999	0.958691
300.000000	5.099998	0.957845
300.000000	5.199998	0.956999
300.000000	5.299997	0.956152
300.000000	5.399997	0.955304
300.000000	5.499996	0.954455
300.000000	5.599996	0.953605
300.000000	5.699995	0.952755
300.000000	5.799994	0.951903
302.000000	4.900000	0.960518
302.000000	4.999999	0.959695
302.000000	5.099998	0.958872
302.000000	5.199998	0.958048
302.000000	5.299997	0.957224
302.000000	5.399997	0.956398
302.000000	5.499996	0.955572
302.000000	5.599996	0.954745
302.000000	5.699995	0.953917
302.000000	5.799994	0.953089

	PRESSURE	Z
401.000000	4.900000	0.984949
401.000000	4.999999	0.984637
401.000000	5.099998	0.984324
401.000000	5.199998	0.984010
401.000000	5.299997	0.983697
401.000000	5.399997	0.983384
401.000000	5.499996	0.983071
401.000000	5.599996	0.982758
401.000000	5.699995	0.982444
401.000000	5.799994	0.982131
403.000000	4.900000	0.985210
403.000000	4.999999	0.984902
403.000000	5.099998	0.984594
403.000000	5.199998	0.984286
403.000000	5.299997	0.983978
403.000000	5.399997	0.983670
403.000000	5.499996	0.983362
403.000000	5.599996	0.983054
403.000000	5.699995	0.982746
403.000000	5.799994	0.982438
405.000000	4.900000	0.985463
405.000000	4.999999	0.985160