

**A NEW COMPUTER MODEL FOR EQUILIBRIUM DATA IN
H₂S-CO₂-AQUEOUS MONOETHANOLAMINE SOLUTION SYSTEMS**

S. N. Lattas *, N. C. G. Markatos †

A new computer-based model for the equilibrium data for the H₂S-CO₂-aqueous monoethanolamine (MEA) solution systems is described. It is based on about one thousand (1000) published experimental equilibrium data points and enables increased accuracy in a wide range of engineering applications. The model is easily implemented on a computer, and needs a minimum calculation time. The program package **PRESS-II**, being the computer implementation of the model, provides the created data base **DAPRE** containing all the experimental data published to date.

INTRODUCTION

The importance of the simultaneous or selective removal of the acid components (H₂S, CO₂, COS etc) from the natural and industrial gases is clear from the many technological solutions that have been developed in practice.

The removal of acid components from such gases is necessary for environmental, technological and financial reasons. The ever-increasing sensitivity of the authorities to limit sulphur compound emissions to the atmosphere, (H₂S, SO_x and other toxic compounds), the poisoning of catalysts and the corrosion of installations, are some of the problems that impose gas purification. Furthermore acid gas recovery to produce S, H₂SO₄, CO₂, etc. establishes gas purification as a financially advantageous process. In particular the reinjection of CO₂, recovered from sour associated or natural gas, into reservoir formations, enhances oil or gas recovery.

The most-applied gas sweetening process is the GIBBOTOL process (1,2,3), used in hundreds of installations all over the world. The process is based on absorption through chemical reaction into aqueous ethanolamine solutions of the acid components contained in gases. The ethanolamines react chemically with H₂S and CO₂ as well as with COS, CS₂ and RSH (mercaptans).

* Asprofos Engineering S.A., 50 Venizelou Av., 176 76, Athens.
† Dep. of Chem. Eng., National Technical University of Athens.

The most commonly used amine is the monoethanolamine (MEA). Its primary advantage is that it reacts with all the acid compounds without selectivity. Since MEA is a stronger base than other ethanolamines, it is the most reactive and consequently involves lower operating cost.

Although this process is the oldest (1930), it is widely used and continues to concern the researchers up to the present day (more than 200 references during the last 5 years).

Most of the industrial amine sweetening units in use today are empirically designed. Stringent limits on the acid compounds content in the gas leaving the top of an absorber (less than 1 ppm H₂S or from 0 to 10 ppm CO₂ for some chemical processes), as well as the change in operating conditions along the aqueous amine solution regeneration column, lead some times to gross over design (with unjustifiably increased cost). In contrast, inadequate design may lead to serious corrosion problems, in addition to other operating difficulties.

For rigorous design of gas sweetening units a complete knowledge of the equilibrium data is needed. The data must cover the whole region of operating parameters of the industrial units, for H₂S, CO₂ or both acid compounds, when they coexist in the sour gas. (As it is well known, there is an interaction in the behaviour of the two acid components during the absorption regeneration process. This interaction strongly depends on their solution concentrations and their proportion).

EQUILIBRIUM DATA

Equilibrium data for the systems H₂S -aqueous MEA solution or CO₂ - aqueous MEA solution as well as for the systems H₂S-CO₂ - aqueous MEA solution have already been presented in the literature, as tables of experimental data, smoothed curves, nomographs or correlation equations. The equilibrium partial pressure of either acid gas is a function of temperature, of amine loading with hydrogen sulphide, and/or carbon dioxide, and of amine concentration in the liquid phase.

Several investigators have measured hydrogen sulphide and carbon dioxide solubility in aqueous MEA solution. Such experimental determinations are difficult to make and, as would be expected, there are differences in the values reported. Among the investigations into H₂S solubility in aqueous MEA the measurements of (4) to (14) have been noted. Similarly for CO₂ in MEA, references (8), (9) and (11) to (20) provide experimental data. Several workers have undertaken studies of the combined absorption of both H₂S and CO₂ and among these are (5), (8), (9), (12), (13), (14), (21) and (22).

Although a great number of investigators have measured the solubilities of the acid gases in aqueous monoethanolamine solutions, the data available are restricted and of limited utility for engineering design. The amine concentration (solution normality) and, in some cases, the temperature ranges

of the data are too narrow, the data in many ranges are meagre or scattered or are inconsistent with other independent studies or the data are for only hydrogen sulphide or only carbon dioxide, but not for mixtures of the two acid gases. Thus, for the conditions in a refinery fuel gas sweetening unit (23), where the absorber operates with a 20 wt % (3.3 N) MEA solution at 40°C and the solution concentration in the regenerator varies between 2.8 and 3.3 N (an usual case in practice), experimental data are not reported (low and very low partial pressures). In addition, because such experimental determinations are difficult to make, especially at high temperatures or low partial pressures, there are differences in values reported for identical or nearly identical runs or as between different investigators.

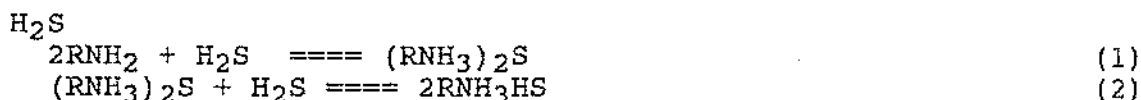
However, in most cases the authors have reported smoothed data or created smoothed equilibrium curves, for individual amine concentrations, from the original experimental data but these equilibrium curves are of limited value when plotted on semi-log scales as is traditionally done. The curves become essentially vertical lines when acid gas loading is low (less than 0.01 mole acid gas / mole MEA) as used in most commercial units in order to meet treated gas quality specifications. Besides, because of the differences in amine concentrations, direct graphical comparisons cannot be made. The need for data at conditions typical of the MEA unit operation was covered (graphically) by Chen and Ng, (24). They used the Kent and Eisenberg (25) model and developed nomographs for MEA systems so as to predict partial pressures of H₂S and/or CO₂ with an accuracy within an acceptable range for normal engineering applications.

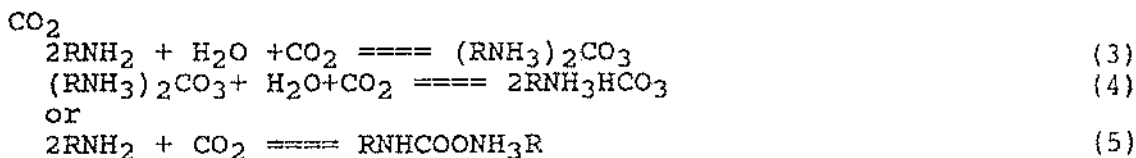
These nomographs can be used for any combination of temperature, concentration and liquid loading within the region of practical gas treating conditions. However, the nomographs cannot be easily implemented for computer calculations needed by modern computer-aided design techniques.

CHEMICAL EQUILIBRIUM MODELS

A number of workers have attempted to correlate and predict the partial pressures of the acid gases above ethanolamine solutions. All the previous attempts postulate the fact that certain chemical reactions occur in solution and propose a thermodynamic model for the reaction equilibria.

Starting from the general reaction form (where R is the -C₂H₅O group in MEA):





a number of possible reaction mechanisms have been proposed considering primary or secondary, irreversible or intermediate reactions occurring in parallel with ionic dissociations and physical solution. Based on the Danckwerts and McNeil studies (26) the Klyamer, Colesnicova and Robin (27) and the Kend and Eisenberg (25) models extended by Vaz (28) are the most recently proposed and they allow for the estimation of equilibrium, with increased accuracy over ranges of temperature, pressure and composition where no experimental data exist. They provide a consistency that is impossible to achieve when graphs must be read manually. In addition, they allow for estimation of properties that have not been measured experimentally.

It seems that only the computer time needed for the model's solution remain as a problem. The thirteen nonlinear equations system (with thirteen unknowns), as originally proposed, must be solved. A recent transformation in an equivalent three expressions system needed an iterative numerical procedure (a modified Newton - Raphson method). In both cases a great number of calculations must be performed.

Consequently a straightforward numerical representation of the experimental data has been developed.

A NEW COMPUTER MODEL FOR EQUILIBRIUM DATA PREDICTION

First an experimental data collection was made. Data extracted from smoothed curves and the Chen and Ng (24) monographs was added to the experimental data collection to complete the regions where no experimental data exist or the existing data are meagre or scattered. Based on the Ostle (29) algorithm, a statistical computer package "REGRESS" (30) was created, containing the appropriate methods for multiple and polynomial regression analysis. Using the computer package "REGRESS" a new model was elaborated. This permits the prediction, with increased accuracy, of the equilibrium partial pressure, for either acid gas, over the $\text{H}_2\text{S} - \text{CO}_2$ - aqueous MEA solution system. The computer implementation of this model is very simple while the equilibrium data calculations needed reduced computer time.

The acid gas partial pressures are expressed in terms of two "correlating variables" K and L. The K variable represents the effect, on the H_2S or CO_2 partial pressure, of the MEA solution loading with either acid gas (mole a.g. /mole MEA). The L variable represents the influence of the MEA solution concentration and temperature on the acid gas partial pressures. Figures 1, 2 and 3 show the dependence on the H_2S partial pressure, of the temperature T, the solution concentration C and the acid gas solution loadings R (H_2S) and Q (CO_2), through the "correlating variables" K_R and L_R .

The curves in Figure 1 were developed using temperature of 50°C and a MEA solution concentration of 20 wt % as reference conditions. Passing from the reference conditions to any desired conditions of temperature and concentration is based on the assumption that the effects of the K_R and L_R "correlating variables" on acid gas partial pressures are practically independent of each other. This assumption is valid in the acid gas loading region between 0.04 and 0.4 mole a.g./mole MEA which covers the most practical region in the gas purification industry. Outside of these loading limits correction procedures must be applied for accuracy improvement.

A reduction in complexity of the model relationships and higher accuracy was obtained by dividing the acid gas loadings variation interval (R [0.001 ; 1.0], Q [0.001 ; 10], Figure 1) into subdomains. Figure 4 indicates the interval division for H_2S partial pressure calculations. A similar division is made for CO_2 partial pressure calculations. In every section, shown in Figure 4, H_2S partial pressure, P_{H_2S} , expressed in mbars, can be calculated from the equation:

$$\log P_{H_2S} = -6.21749 + 0.4054 K_R + 0.20754 L_R \quad (6)$$

where :

$$L_R = -1.155 + 5.149 \log C + 0.0976 T \quad (T \geq 70^\circ C) \quad (7)$$

$$K_R = 30.53 R^{0.362}, \quad (8)$$

when $Q=0$ and $R \in [0.001 ; 0.01]$. In the region $R \in [0.01 ; 0.1]$ and $Q \in [0.1 ; 0.5]$:

$$K_R = K_{Q=0.1}(R) + \Delta K(Q) \quad (9)$$

where :

$$K_{Q=0.1}(R) = 16.035 R^{0.143} \quad (10)$$

$$\Delta K(Q) = -1.22 + 14.46 Q - 26.6 Q^2 + 37.49 Q^3 \quad (11)$$

The values of the "correlating variables" K_R and L_R for the remaining subsections (of the R , Q , T variation interval) can be calculated from similar relationships (31), (32).

In a similar way the dependence of the CO_2 partial pressure from the temperature, concentration and acid gas loadings through the use of the "correlating variables" K_Q and L_Q , is expressed (in mbars) as follows :

$$\log P_{CO_2} = -7.4236 + 0.4166 K_Q + 0.2104 L_Q \quad (12)$$

where :

$$L_Q = 1.12 + 0.242 \log C + 0.1755 T \quad (13)$$

$$K_Q = 2.84 + 163.7 Q - 1771.5 Q^2 - 7905.9 Q^3 \quad (14)$$

when $R=0$ and $Q \in [0.01 ; 0.1]$. In the region $R \in [0.01 ; 0.1]$ and $Q \in [0.01 ; 0.1]$:

$$K_Q = K_{R=0.01}(Q) + \Delta K(Q) r_K(R) \quad (15)$$

where :

$$K_{R=0.01}(Q) = 17.89 Q^{0.28} \quad (16)$$

$$\Delta K(Q) = 2.66 - 0.029 \sqrt{Q} \quad (17)$$

$$r_K(R) = -0.494 + 4.78 \sqrt{R} \quad (18)$$

Similar relationships permit acid gas partial pressure predictions within the other regions of MEA solution loadings (31).

CORRECTION FACTORS FOR ACCURACY IMPROVEMENT

The accuracy of the results is acceptable for the usual design and other engineering calculations mainly, when the equilibrium parameters lie in the region of the operating conditions, met in the industrial gas purification units. If increased accuracy is needed a correction procedure must be applied, using the correction equations (similar to these proposed by Chen and Ng (24), but extended to obtain a better fit to the experimental data):

$$P_{H_2S}^C = P_{H_2S} f_T (0.18T-8.8)(0.05C)^{f_C} f_R \quad (19)$$

$$P_{CO_2}^C = P_{CO_2} f_T (0.18T-8.8)(0.333 \ln C)^{f_C} f_Q \quad (20)$$

The correction factors f_T , f_C and f_R , for the H_2S partial pressure, are shown in Figures 5, 6 and 7 as functions of the MEA solution loadings R and Q (with acid gas). Similar figures for the CO_2 partial pressure correction factors are given in a recent work (31). Incorporation of the correction procedure in the model, for computer implementation purposes, was realized through development of appropriate equations. The correction factor expressions cover the whole loading variation range from 0.001 to 1 mole a.g./mole MEA. When additional physical absorption is covered, the loadings range can be extended up to 2 moles a.g./mole MEA.

A further reduction in the complexity of the equations and additional accuracy was obtained by dividing the acid gas loadings variation range into sections. Figure 8 indicates the interval division for f_T and f_C calculations for H_2S ,

where, for example, if $R+2Q > 1.4$ (region VII from Figure 8), f_T can be calculated as :

$$f_T = 0.84 - 0.02 R - 0.004 Q \quad (21)$$

when $R \in [0 ; 1]$ and $Q \in [0 ; 0.05]$ (regions I and V), f_C can be calculated as:

$$f_C = (0.15 - 0.26 R^{0.33})^3 / (1-e^{-Q}) \quad (22)$$

In the region II where $R + 2 Q < 0.6$ and $Q \in [0.05 ; 0.1]$:

$$f_T = 1 \quad (23)$$

$$F_C = 0 \quad (24)$$

In the region of low solution loadings ($R, Q, \in [0.0 ; 0.1]$) improved H_2S partial pressures can be obtained using the following expression for f_R calculation :

$$f_R = 1.1 + 15.2 R - 163R^2 \quad (25)$$

Similar relationships permit the f_T , f_C , f_R , f_Q calculations within the remaining regions of MEA solution loadings depending on the predicted H_2S partial pressures as also on the whole region of predicted CO_2 partial pressures (31).

The use of the correction procedure becomes necessary only when the liquid loadings pass outside the region 0.04 and 0.4 moles a.g/ mole MEA and the temperature or solution concentration is far away from the reference conditions ($50^\circ C$ and 20 wt %). Only the f_R and f_Q correction factors are applicable irrespective of temperature and concentration values.

Generally, for normal industrial application purposes, when the solution loadings lie into the dark zone, Figure 9, the use of the correction procedure (f_T and f_C) is not needed and the model becomes simpler. Only when advanced solution purification is practised and increased accuracy is needed does the correction procedure become necessary (because the MEA solution loadings violate the lower limit of the above interval - the upper loadings limit is practically never exceeded to avoid corrosion acceleration).

It is especially true that for the f_R and f_Q application a compromise between desirable accuracy and complexity of the model determines the region where these correction factors should be applied.

THE COMPUTER PACKAGE "PRESS - II"

Based on the previously presented new correlation model, the computer program PRESS-II was developed. This program is able to perform H₂S and/or CO₂ partial pressure calculations in the systems H₂S and/or CO₂-aqueous monoethanolamine solution over the whole range of temperature, concentration and solution loadings.

In its general configuration the computer package PRESS-II, written in FORTRAN IV of single and double precision, consists of 3 independent main programs, the library PRESS containing 8 subprograms and the data base DAPRE. The main programs PREINT, PREFIL and PREDAP correspond to different input modes. While PREFIL utilizes a user-created input file and the PREDAP uses as input file the data base DAPRE, the main program PREINT permits the user to choose between the three possible modes, i.e. the interactive mode, the user created input file mode and the input from the data base mode.

The subroutines PRESSRQ, PRESSR, PRESSQ contain the implemented equilibrium model for H₂S and CO₂ partial pressure calculations when both acid gases coexist in equilibrium or for the other two particular simplified modes (only H₂S or CO₂ respectively). The subroutines CORRER and CORREQ called from the previous subroutines perform the calculated H₂S and CO₂ partial pressure corrections respectively. The routines PRESSRQS, PRESSRS and PRESSQS contain quick simplified versions of the equilibrium model without calling on the correction subroutines (for real time calculations purposes). This procedure is of sufficient accuracy for common industrial and other practical applications.

Thus PRESS-II, having as input data the aqueous solution concentration C in MEA weight percent, the solution temperature T in °C and the solution loadings R and Q as moles H₂S/mole MEA and moles CO₂/mole MEA respectively, computes and furnishes the H₂S and CO₂ partial pressures P_{H₂S} and P_{CO₂} (in the system H₂S-CO₂-MEA-H₂O) according to the block diagram in Figure 9.

In this way the PRESS-II package serves as an equilibrium data generator (data base), furnishing the H₂S and/or CO₂ equilibrium partial pressures in the system H₂S and/or CO₂-aqueous MEA solution. Thus it can be used by simulation programs to generate (i.e. for process design, optimization or process control of a gas sweetening unit using MEA), the indispensable equilibrium data for H₂S and CO₂. For such uses it is possible to incorporate the PRESS library or the subroutines only needed into the simulator (33).

The calling sequences from the simulation program to use the PRESS-II calculation procedure are quite similar both in appearance and in the roles their arguments play for every one of the previous subroutines, i.e. :

```
CALL PRESSRQ (R, Q, C, T, PH2S, PCO2)
```

In addition, if the experimental (measured) partial pressure values P^E_{H₂S} and/or P^E_{CO₂} are given as input data, Figure 9, the program compares the calculated with the experimental values giving


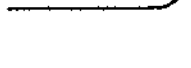
the differences DP_{H_2S} and/or DP_{CO_2} as also the percent deviation between the calculated and experimental values ($\% DP_{H_2S}$ and/or $\% DP_{CO_2}$) needed to assess the accuracy of the correlation.

Running the equilibrium data generator needs a very small computer CPU time. When the complete version is used (data transmission to proper subroutines, H_2S and CO_2 partial pressure calculations, correction procedure application and results return to the calling routine) the computer CPU time is about 0.008 s per calculated case or 0.8 s per one hundred calculations on a CDC Cyber 171 computer. When the partial pressure calculations are made for systems where only H_2S or CO_2 exist the computer CPU time is 0.005 s per calculated case. If the simplified versions are used for practical simulation purposes (gas purification unit design, operation or control) when the correction procedure is not generally needed, the computer CPU time becomes minimal and is below 0.004 CPU s per equilibrium point calculation. Especially when only one acid gas is present the CPU time spent can be less than 0.002 s per case.

A complete operation with PRESS-II, i.e. data input, H_2S and CO_2 partial pressure calculations, $\% DP_{H_2S}$ and $\% DP_{CO_2}$ calculations and result typing, requires 2 CPU s per one hundred different equilibrium points.

TABLE 1 - The Equilibrium Data Base "DAPRE"

R	Q	C	T	$P_{H_2S}^E$	$P_{CO_2}^E$				
moles H_2S mole MEA	moles CO_2 mole MEA	wt % MEA	(+)	(*)	(*)				(*) pressure unit index (+) temperature unit index
.0	.244	15.5	100.	0.	32.6	1	2	30	MUHLBAUER-MONAGHAN
.0	.200	15.5	100.	0.	18.7	1	2	30	MUHLBAUER-MONAGHAN
.0	.165	15.4	100.	0.	13.4	1	2	30	MUHLBAUER-MONAGHAN
.0	.136	15.4	100.	0.	8.1	1	2	30	MUHLBAUER-MONAGHAN
.0	.2	12.2	140.	0.	550.	3	2	29	REED-WOOD
.0	.27	12.2	140.	0.	1000.	3	2	29	REED-WOOD
.0	.368	12.2	140.	0.	2000.	3	2	29	REED-WOOD
.714	.0	12.2	15.	20.	0.	3	2	28	LEIBUS-SNEERSON
.83	.0	12.2	15.	40.	0.	3	2	28	LEIBUS-SNEERSON
.9	.0	12.2	15.	60.	0.	3	2	28	LEIBUS-SNEERSON
.0420	.0462	15.3	100.	.561	.126	5	2	33	ISAACS-OTTO-MATHER
.0425	.0457	15.3	100.	.778	.135	5	2	33	ISAACS-OTTO-MATHER
.0459	.0085	15.3	100.	.391	.0048	5	2	33	ISAACS-OTTO-MATHER
.0504	.0593	15.3	100.	.823	.220	5	2	33	ISAACS-OTTO-MATHER
.0507	.0610	15.3	100.	.752	.211	5	2	33	ISAACS-OTTO-MATHER

index of the literature source 
name of investigators (authors) 

THE EQUILIBRIUM DATA BASE "DAPRE"

The data base DAPRE contained in the computer package PRESS-II summarizes all experimental equilibrium data known to date for the systems H_2S and/or CO_2 -MEA- H_2O (up to 1000 sets of data). To supplement this data base contains some smoothed data extracted from published curves.

The data base configuration is shown in Table 1. Besides the already discussed values of R , Q , C , T , $P^{E_{H_2S}}$, $P^{E_{CO_2}}$ per equilibrium point, the data base contains indicators for the temperature and pressure units (as reported from the previous investigators) and literature information.

This data collection is very interesting because it is complete, accessible from the program and it can be easily used mainly for correlation verification and further improvement.

VERIFICATION OF THE NEW CORRELATION'S ACCURACY

For accuracy verification of the results of the new model of correlation (provided by the computer package PRESS-II) a comparison is made against all the published experimental data. In addition, a cross check is made between predicted data by the new model and data resulting from other published prediction models. A complete set of figures showing the comparison with all these data is contained in a recent work (31).

Figures 10, 11, and 12 show a comparison of H_2S partial pressures predicted by the present model against a great number of published experimental data in the system H_2S -aqueous MEA solution. These data cover a wide range of MEA concentrations (from 5 to 30.2 wt%), solution temperatures (from 15 to 140°C) and H_2S loadings. Comparisons for the CO_2 -aqueous MEA solution systems are shown in Figure 15, while Figures 13 and 14, as well as, Table 2 show the comparison between predicted and experimental data in the systems H_2S - CO_2 -MEA- H_2O . It must be mentioned that all these values predicted by PRESS-II are created without using the correction factors f_R and f_Q , except for Figures 11, 15 (for H_2S only) and Table 2.

Especially, in Figures 15 and Table 2 a comparison is made between the present model (PRESS-II) and the models of Kent and Eisenberg (25), Klyamer et.al. (26) and Vaz (28). In this case the predicted equilibrium data are compared against published experimental or smoothed data. A careful examination of these data indicates a generally good agreement between the new model of correlation and the experimental determinations. This conclusion is based on:

- The new model fits the experimental data with increased accuracy in a region that covers the common practical regions of variation of the operating parameters, met in industrial gas purification units.

TABLE 2 - Comparison of the present work with other equilibrium models and experimental data at low acid gas partial pressure at 2.5N MEA solution and 100°C.

CO ₂ Moles mole	H ₂ S a.g. MEA	Vaz (28)	Kent- Eisenberg from(14)	Klyamer from(14)	Present Work PRESS-II	Smoothed val.from Isaacs(14)	Other
P_{H_2S} (mbars)							
0.0	0.02	0.5	0.5	0.7	0.8	0.4	0.5 (24)
	0.06	5.1	4.4	4.9	6.	7.	12.3 (12)
	0.1	15.	10.	13.	14.	18.	33. (12)
0.02	0.02	1.2	1.	1.1	1.5	0.7	0.5 (14)
	0.06	7.2	6.2	6.4	7.	8.3	
	0.1	18.8	16.	15.	14.7	22.	
0.06	0.02	2.5	2.1	2.2	3.3	2.	
	0.06	12.	10.	9.6	9.1	11.	>9.3 (14)
	0.1	27.8	23.	21.	18.1	28.	
0.1	0.02	4.2	3.5	3.3	4.7	3.	
	0.06	17.6	15.	13.	21.3	17.	15.8 (14)
	0.1	38.4	32.	26.	33.5	37.	35. (24)
P_{CO_2} (mbars)							
0.02	0.0		0.1	0.2	0.1	<0.01	>0.03 (8)
	0.02	0.1	0.2	0.4	0.2	0.1	0.1 (14)
	0.06	0.3	0.4	0.8	0.4	0.5	
	0.1	0.4	0.6	1.2	0.7	0.9	
0.06	0.0	0.5	0.9	2.	0.9	0.4	
	0.02	0.7	1.2	2.6	1.3	1.1	
	0.06	1.	2.	4.	2.1	2.5	>2.5 (14)
	0.1	1.6	3.	5.	3.	3.5	
0.1	0.0	1.6	3.	6.	3.1	1.9	1.6(14,8)
	0.02	2.	3.7	7.1	3.9	3.3	
	0.06	2.9	5.5	9.6	5.8	5.8	>5.2 (14)
	0.1	4.1	7.5	12.	7.5	7.6	6.8 (24)

TABLE 3 - Some discrepancies in the experimental measurements reported by several investigators

R	Q	C	T	P_{H_2S}	P_{CO_2}	DP	% DP	References
Moles	a.g.	% wt	°C	mbars	mbars			
Mole	MEA							
0.014		15.3	100	0.4		0.31	350	Lawson-Garst (9)
0.016				0.09				Isaacs-Otto-Math(14)
	0.16	15.3	100		8			Jones-Froning-Cl.(8)
	0.164				10.4	2.4	30	Isaacs-Otto-Math(14)
	0.165				17.9	9.9	120	Mahlbauer-Monagh(12)
0.380		15.2	40	12.2				Lawson-Garst (9)
0.373				14.5		2.9	25	Lawson-Garst (9)
	0.050	15.3	100		0.18			Isaacs-Otto-Math(14)
	0.047				0.22	0.05	30	Isaacs-Otto-Math(14)

- In many regions the new prediction model fits the experimental data better than other suggested methods. However in some regions all the prediction models have similar accuracies.
- The overall accuracy on fitting the experimental data depends strongly upon the accuracy of the experimental methods used. Such experimental determinations are difficult to make especially in the low partial pressure or high temperature regions.

As would be expected, there are differences in the experimental values reported by different investigators. Such discrepancies are collected and indicated especially in Table 3, as well as in Table 2 and many of the Figures. Even in many cases duplicate or near duplicate runs, made by some investigators, show a discrepancy of up to 30%.

Further comparison of the predicted data with smoothed reported values is not justified because these values are often based only on individual authors' data and not on a general collection of experimental data. Even further effort on more improvements in the correlation to obtain greater accuracy is not justified because of the scatter in the experimental data.

CONCLUSIONS

It is concluded that a user-friendly and fast computer package has been developed to provide equilibrium partial pressures of H_2S and CO_2 in the system H_2S-CO_2 -aqueous MEA solution. The program performance has been tested against all the experimental data and the data predicted from other models and appears very satisfactory. Thus the PRESS-II computer package can be used as a data generator incorporated into a simulator for sweetening units design and operation purposes.

ACKNOWLEDGEMENTS

The authors wishes to express their gratitude to Hellenic Aspropirgos Refinery, in Athens, for their partial financial support for the work.

SYMBOLS USED

- R = H₂S loading (moles of total H₂S dissolved/mole MEA)
- Q = CO₂ loading (moles of total CO₂ dissolved/mole MEA)
- C = aqueous MEA solution concentration (wt% MEA)
- T = solution temperature (°C)
- K_R, K_Q = "correlating variables" presenting the effect of the acid gas loadings on the H₂S (the K_R) and CO₂ (the K_Q) partial pressures.
- L_R, L_Q = "correlating variables" representing the effect of the temperature and solution concentration (as wt% of MEA) on the H₂S (the L_R) and the CO₂ (the L_Q) partial pressures.
- f_R, f_Q, f_C, f_T = Correction factors depending on H₂S loading, CO₂ loading, solution concentration and solution temperature.
- p, p^C, p^E = acid gas partial pressure - calculated, corrected and measured (mbars).
- $\Delta p, \% \Delta p$ = acid gas partial pressure difference and percent deviation (between measured and predicted values).
- $K_{Q=0.1}(R)$ = the R (H₂S loading) effect on the H₂S partial pressure when Q = 0.1 mole CO₂/mole MEA.
- $\Delta K(Q)$ = the additional effect of the R loading on the H₂S partial pressure due to the excess Q loading (Q - 0.1).
- $K_{R=0.01}(Q)$ = the Q (CO₂ loading) effect on the CO₂ partial pressure when R = 0.01
- $\Delta K(Q)$ = the additional effect of the Q loading on the CO₂ partial pressure due to the additional R loading from 0.01 to 0.1.
- $r_K(R)$ = the ratio between the R loading effect and the maximum R loading (R = 0.1) effect
- MEA = Monoethanolamine.
- ε = The mathematical symbol "belongs"

REFERENCES

1. Bottoms, R.R., (1931) Ind. Eng. Chem, 25(5), 501 .
2. Kohl, A & Riesenfeld, F., (1979) "Gas Purification", 3rd Ed., Gulf Publ. Co., Houston, Texas .
3. Stratula, C., (1984) "Purificarea Gaselor", Edit., Stintifica si Enciclopedica, Bucuresti, Romania
4. Riegger, E., Tartar, H.V., & Lingafelter, E/C., (1944) J. Am. Chem. Soc., 66,2024
5. Leibush, A.G. & Shneerson, A.L., (1950) Zhur. Priklad. Khim., 23,145
6. Atwood, K., Arnold, M.,R. & Kindrick, R.C., (1957) Ind. Eng. Chem., 49 (9), 1439
7. Afanasev, Y.M., Garnova T.G. & Golovatenko, Z.A., (1974) Khim, Prom., 10, 751.
8. Jones, J.H., Froning H.R. & Claytor, E.E., Jr., (1959). J. Chem.Eng. Data, 4 (1), 82
9. Lawson, J.D & Garst, A.W., (1976) J. Chem. Eng Data, 21(1), 20
10. Lee J.I., Otto, F.D. & Mather A.E., (1974) Can.J. Chem Eng, 52(12), 803.
11. Lee, J.I., Otto, F.D. & Mather, A.E., (1976) J. Chem. Eng. Data 21(2), 207.
12. Muhlbauer, H.G.& Monaghan, P.R., (1957) Oil Gas J., 55 (17), 139
13. Nasir, P. & Mather, A.E., (1977) Can. J. Chem. Eng., 55 (), 715
14. Isaacs, E.E., Otto, F.D. & Mather, A.E., (1980) J. Chem. Eng. Data, 25 (2), 118 .
15. Mason, J.W. & Dodge, B.F., (1936) Trans. AIChE, 32, 27 .
16. Atadan, E.M., (1954) Ph.D. Thesis, University of Tennessee.
17. Leites, I.L., Siskova, O.P. & Sinelis, A.F., (1972) Khim. Prom., 8 (4), 263 .
18. Lyudkovskaya, M.A. & Leibush, A.G., (1949) Zhur. Priklad. Khim., 22 (6), 558
19. Murzin, V.I. & Leites, I.L., (1971) Zhur. Fiz. Khim., 45, 2642
20. Reed, R.M. & Wood, W.R., (1941) Trans. AIChE, 37, 363 .

21. Lee, J.I., Otto, F.D. & Mather, A.E., (1975) J. Chem. Eng. Data, 20 (2), 161 .
22. Lee, J.I., Otto, F.D. & Mather, A.E., (1976). Can. J. Chem. Eng., 54 (6), 214
23. U-3500, Operating Manual, Hellenic Aspropyrgos Refinery, Athens (1987).
24. Chen., C.C. & Ng, A., (1980) Hydroc. Proc., 59 (4), 122
25. Kent, R.L. & Eisenberg, B., (1976) Hydroc. Proc., 55 (2), 87.
26. Danckwerts, P.V. & McNeil, K.M., (1967) Trans. Inst. Chem. Eng., 45, T32 .
27. Klyamer, S.D., Kolesnikova, T.L. & Robin Y.A., (1973) Gazov. Prom., 18 (2), 44 .
28. Vaz, R.N., (1980) Ph.D. Thesis, Oklahoma State University, Stillwater, Okla.
29. Ostle, B., (1954) "Statistics In Research", The Iowa State College Press .
30. Lattas, S. N., (1985) "REGRESS - Computer Package for Multiple Polynomial Regression analysis", Reference and User's Guide, Nat. Techn. University Athens .
31. Lattas, S. N., Ph.D. Thesis, Nation. Techn. Univ., Athens (to be submitted 1989).
32. Stratula, C. & Lattas, S.N., (1986) Rev. Chim., 37 (12), 1080
33. Lattas, S. N. & Markatos, N.C.G., Paper to be presented at the CIPE '89 Congress, Leeds (1989).

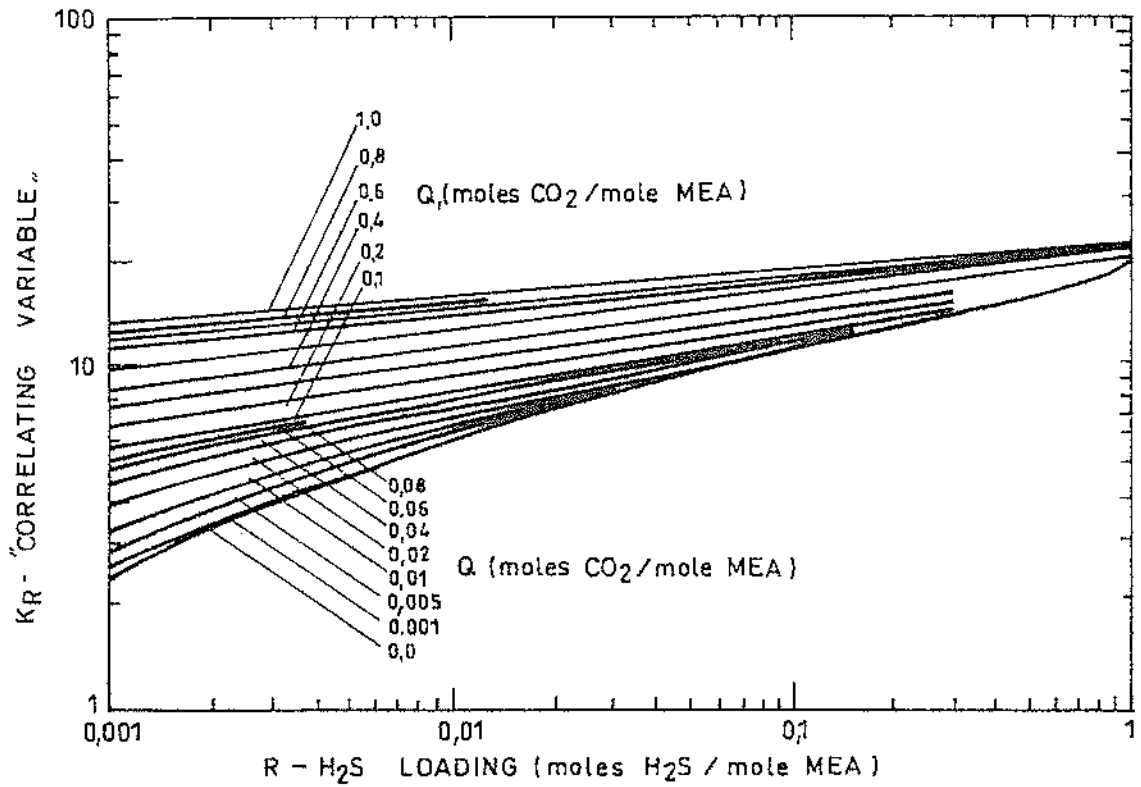


Figure 1 Dependence of the "Correlating variable" K_R on MEA solution loading with H_2S and CO_2 .

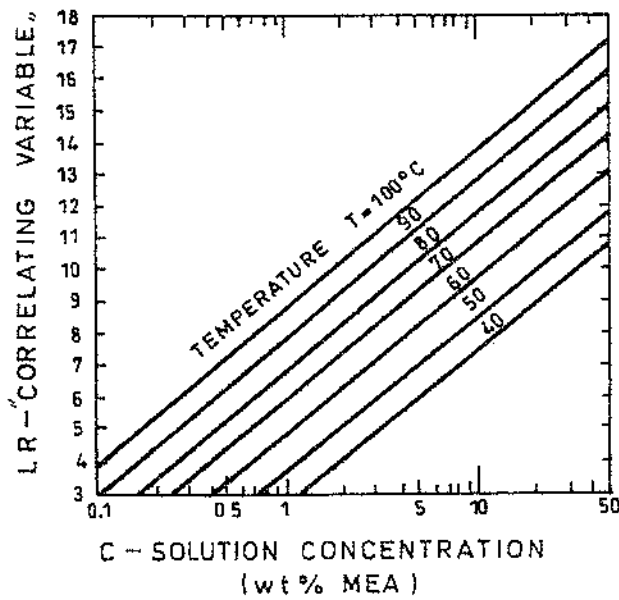


Figure 2 Dependence of the "Correlating variable" L_R on temperature and MEA concentration.

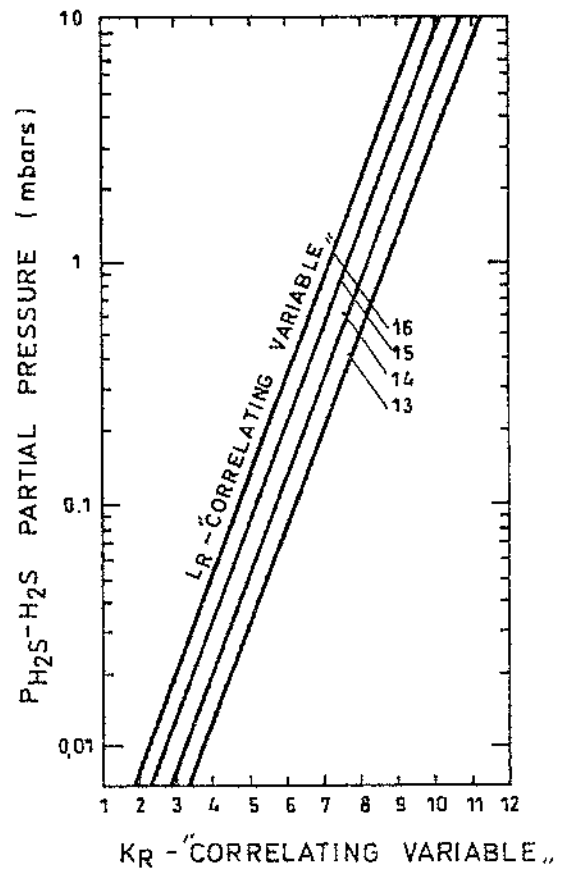


Figure 3 Effect of the "Correlating variables" K_R and L_R on H_2S partial pressure.

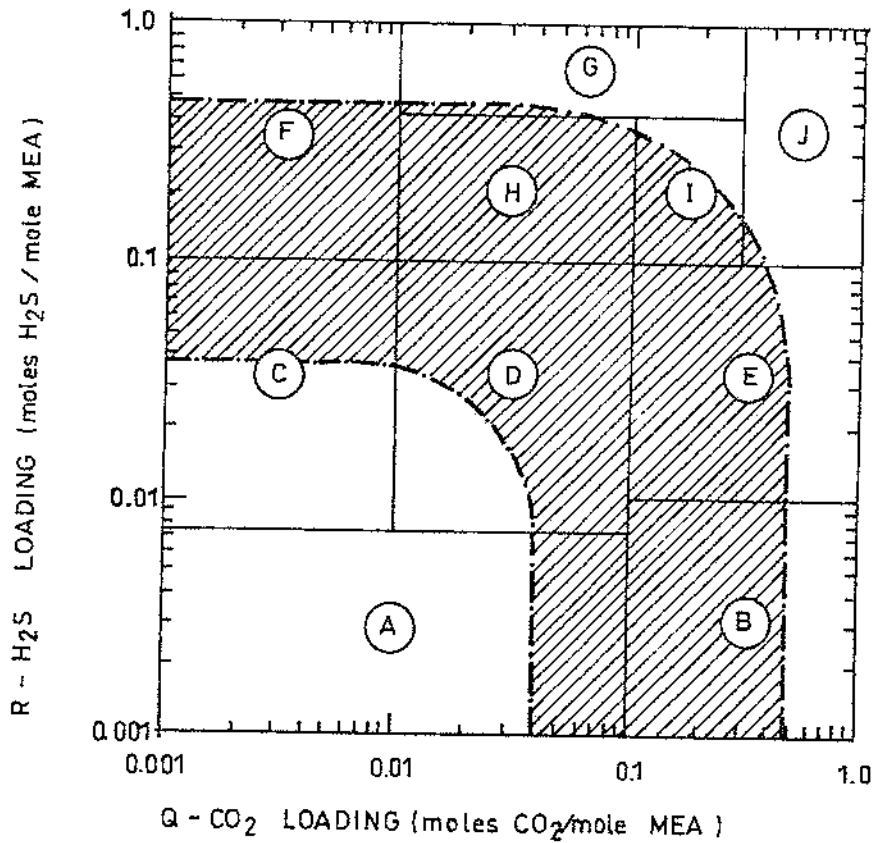


Figure 4 Division of the R and Q variation regions for H_2S partial pressure calculations (dark zone: region of normal industrial applications).

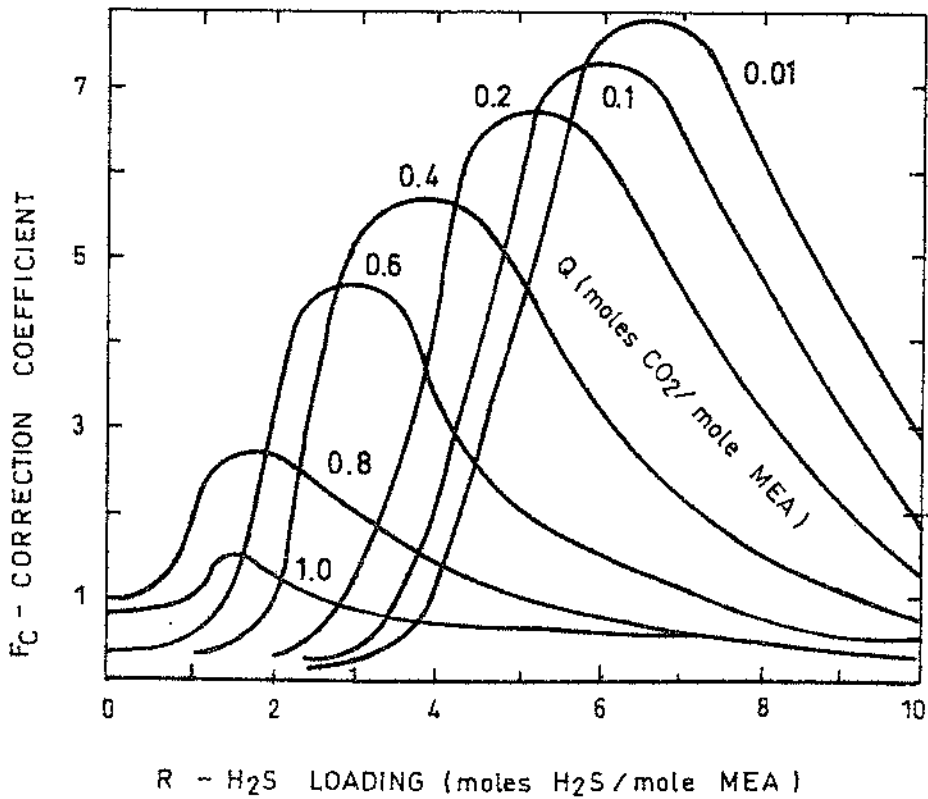


Figure 5 The correction factor f_C (for the H_2S partial pressure calculation) as a function of MEA solution loading with H_2S and CO_2 .

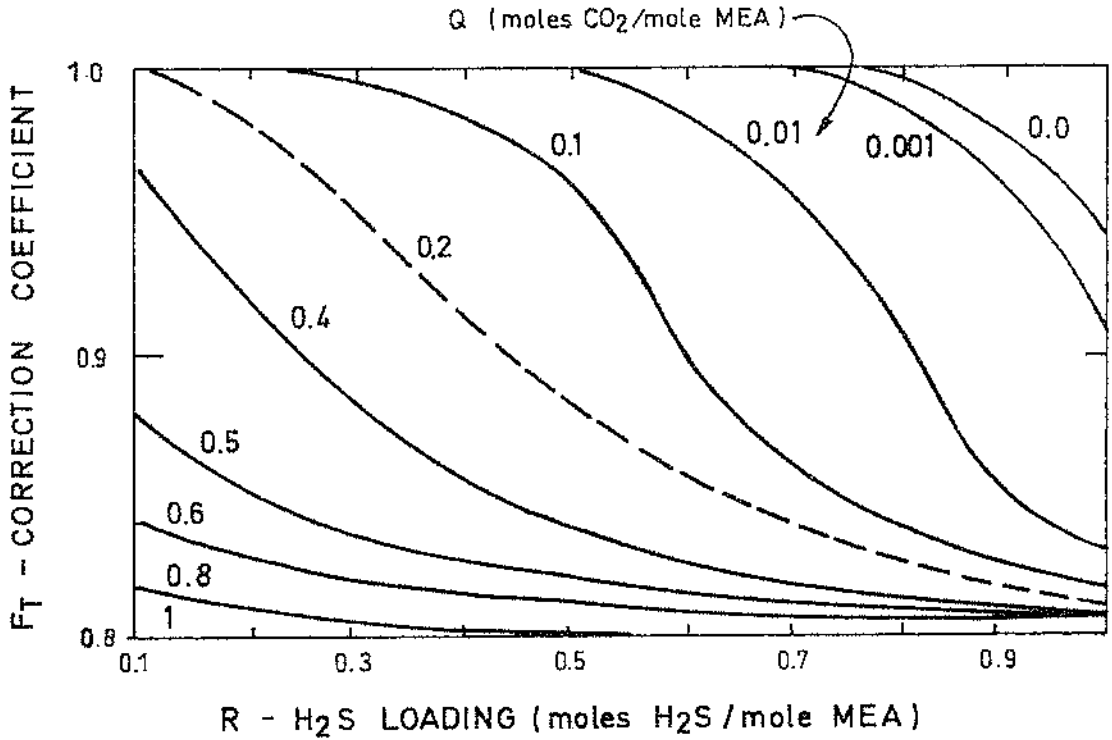


Figure 6 The correction factor f_T (for the H_2S partial pressure calculation) as a function of MEA solution loading with H_2S and CO_2 .

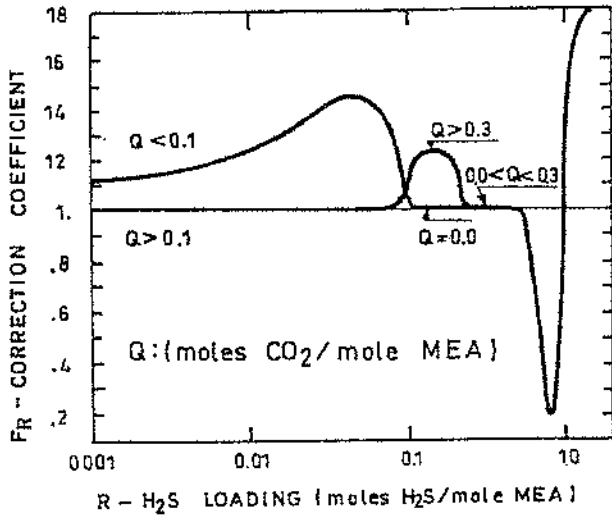


Figure 7 The correction factor f_R for the H_2S partial pressure calculation.

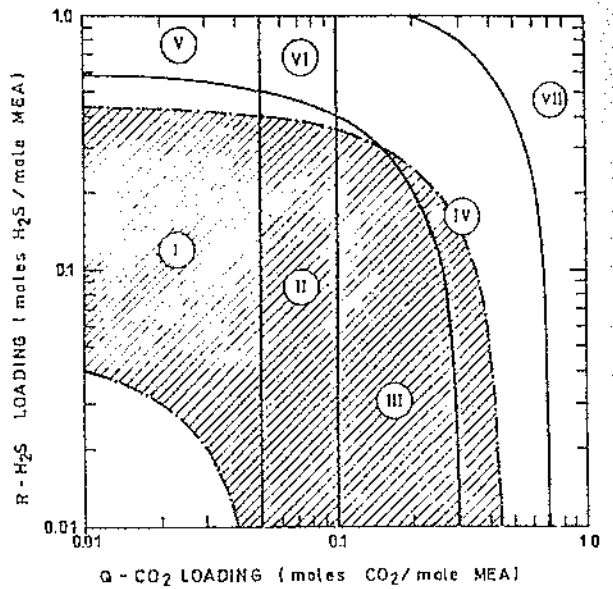


Figure 8 Sections for $f_{H_2S}^C$ correction procedure application. (Dark zone: $f_T=1$, $f_C=0$ (for practical applications))

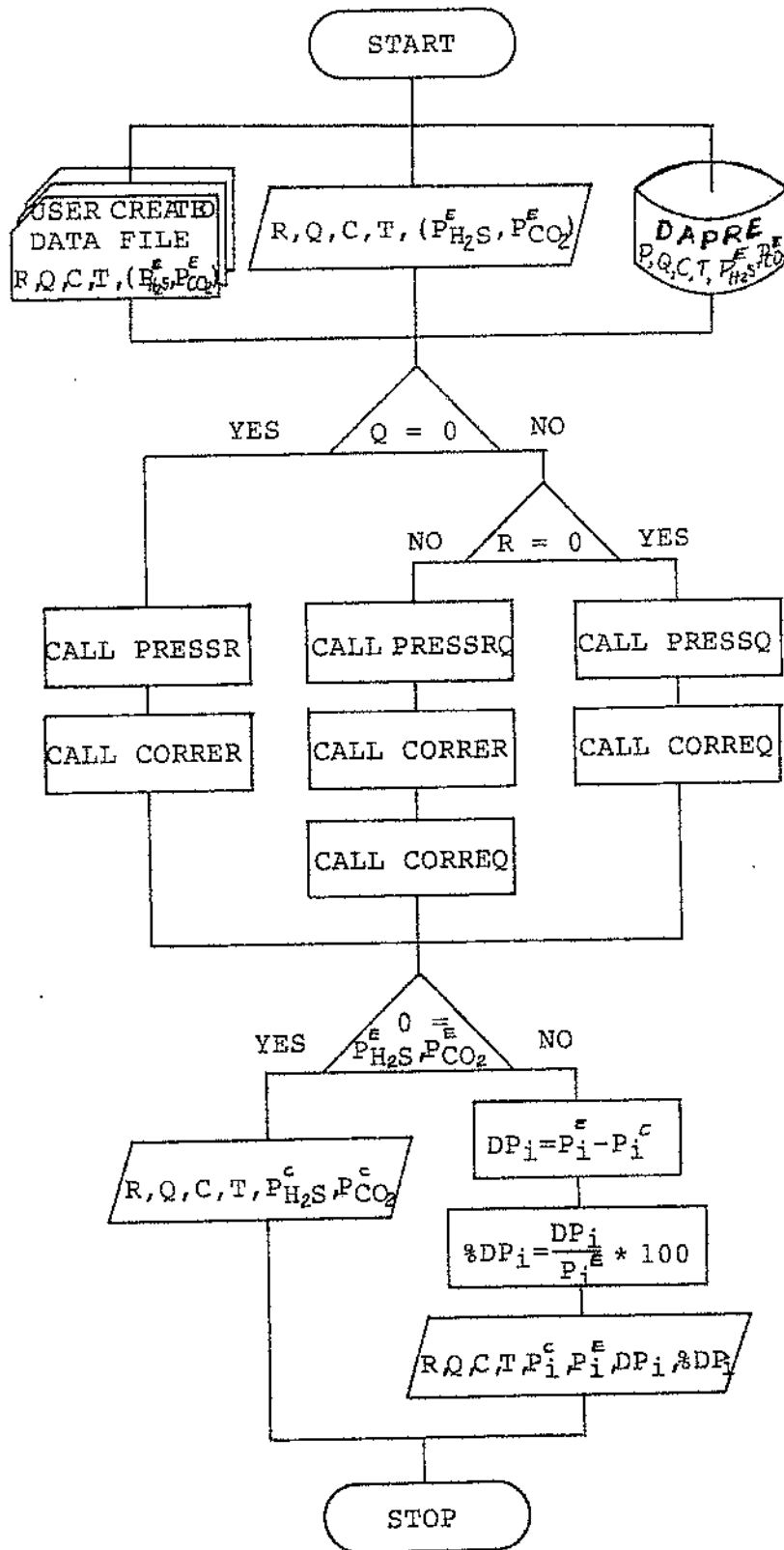


Figure 9 Block diagram of P_{H_2S} and/or P_{CO_2} calculation in the system H_2S and/or CO_2 -aqueous MEA solution using the computer package PRESS-II.

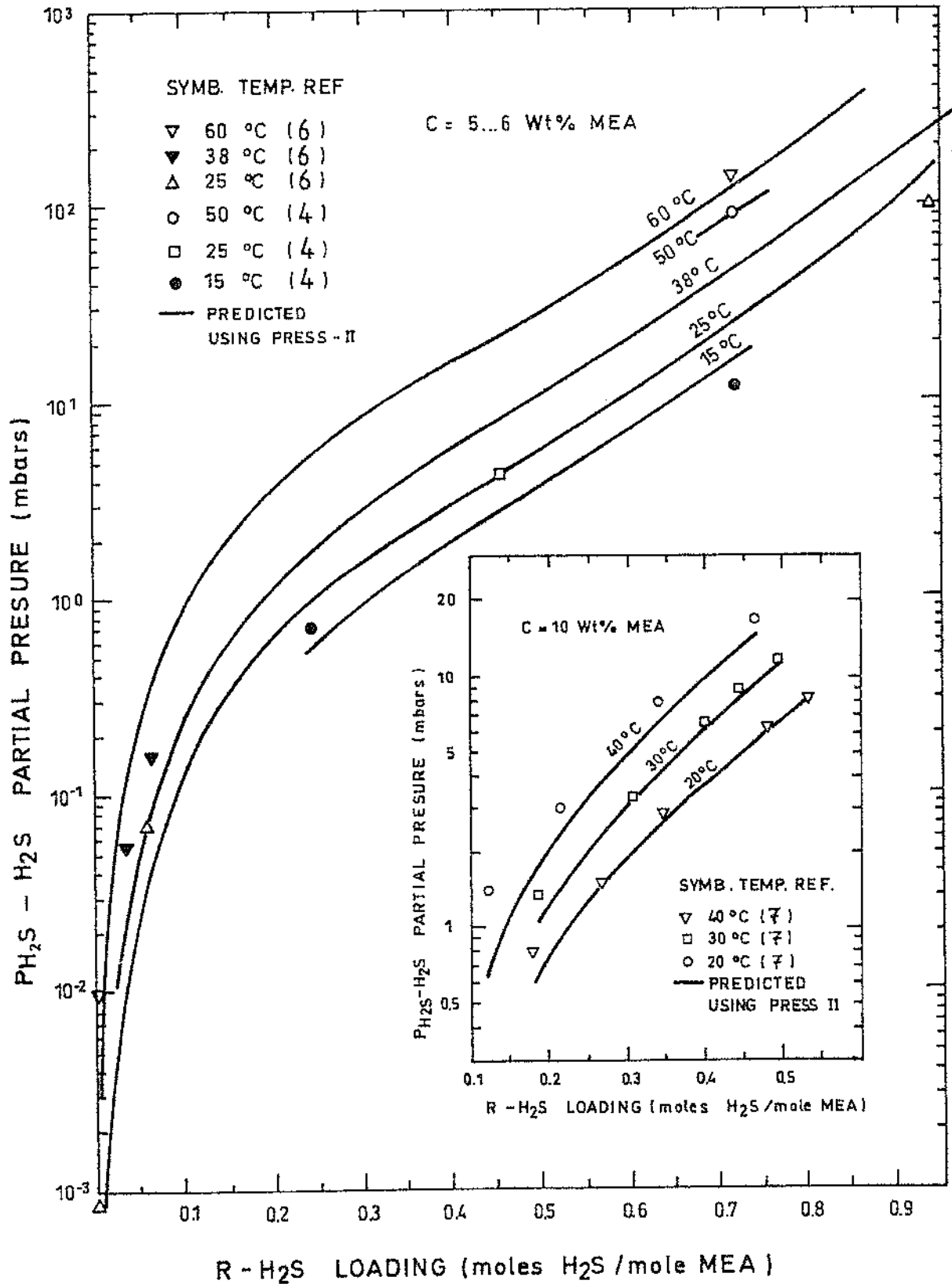


Figure 10 Comparison of experimental and calculated with PRESS-II values of H₂S partial pressure over 5 to 10 wt% MEA solution.

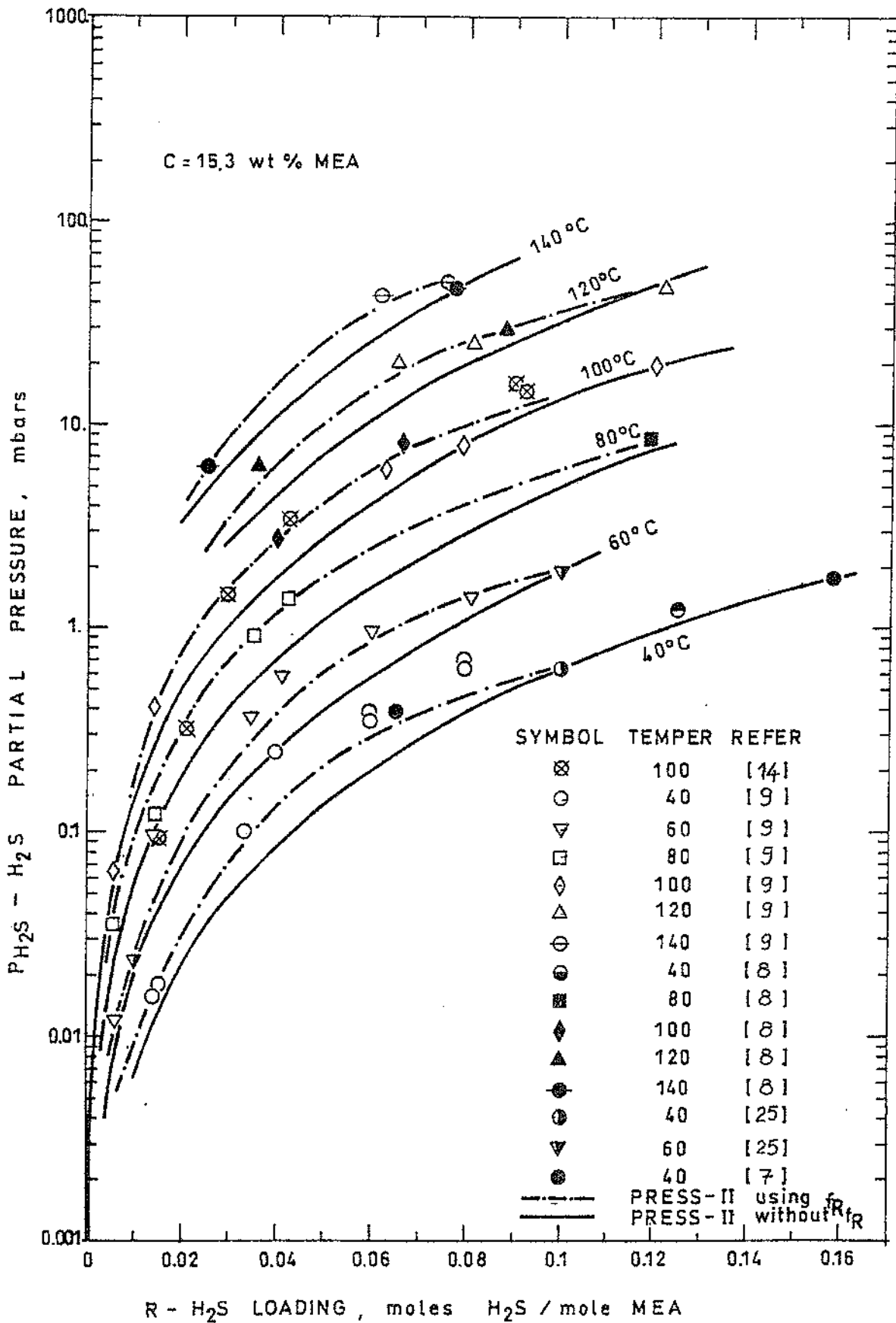


Figure 11 Comparison of experimental and predicted values of H₂S partial pressure, at low solution loadings and 15.3 wt% MEA.

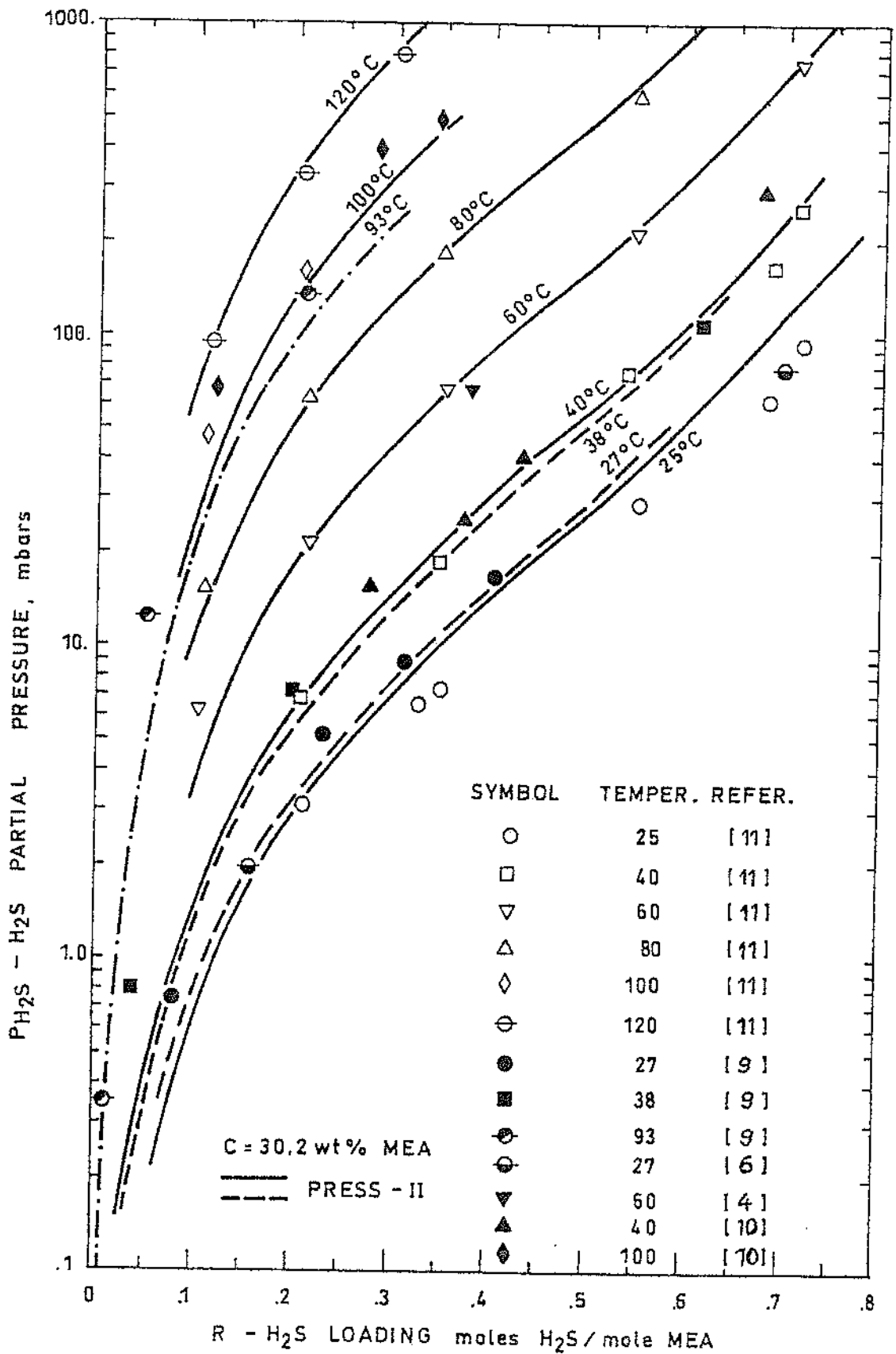


Figure 12 Comparison of experimental and predicted values for H_2S partial, pressure over a 30.2 wt% of MEA solution concentration.

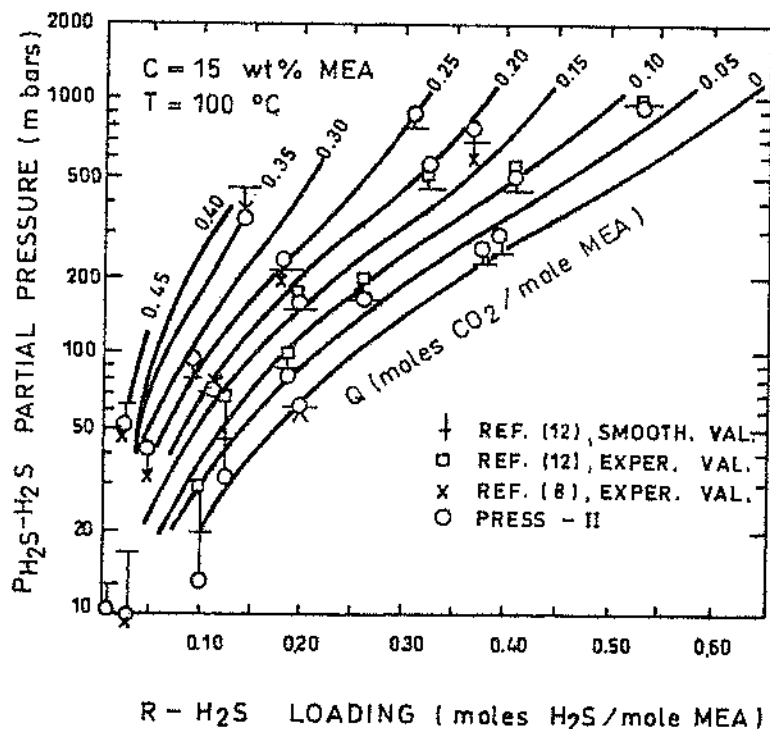


Figure 13 Comparison of the present work with experimental data in the system $\text{H}_2\text{S}-\text{CO}_2$ -aqueous MEA solution at 15.3 wt% MEA and 100°C .

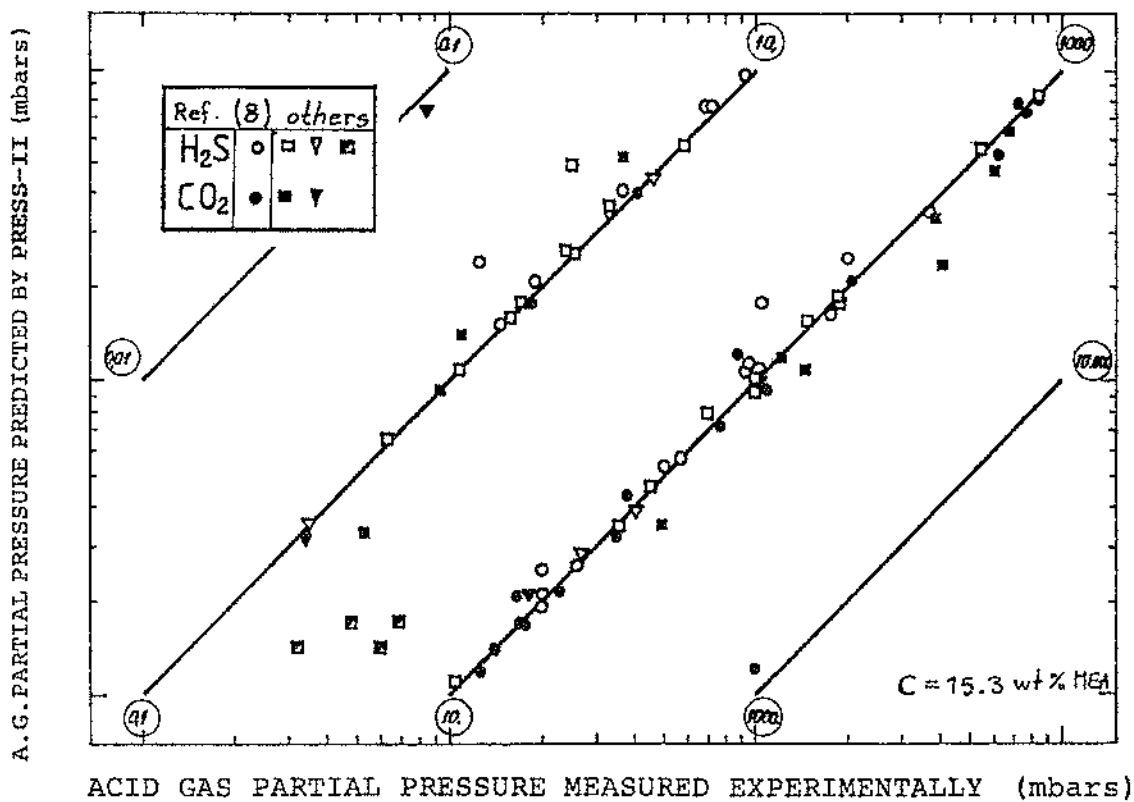


Figure 14 Comparison of predicted by PRESS-II and measured values for H_2S and CO_2 partial pressures over a 15.3 wt% MEA solution.

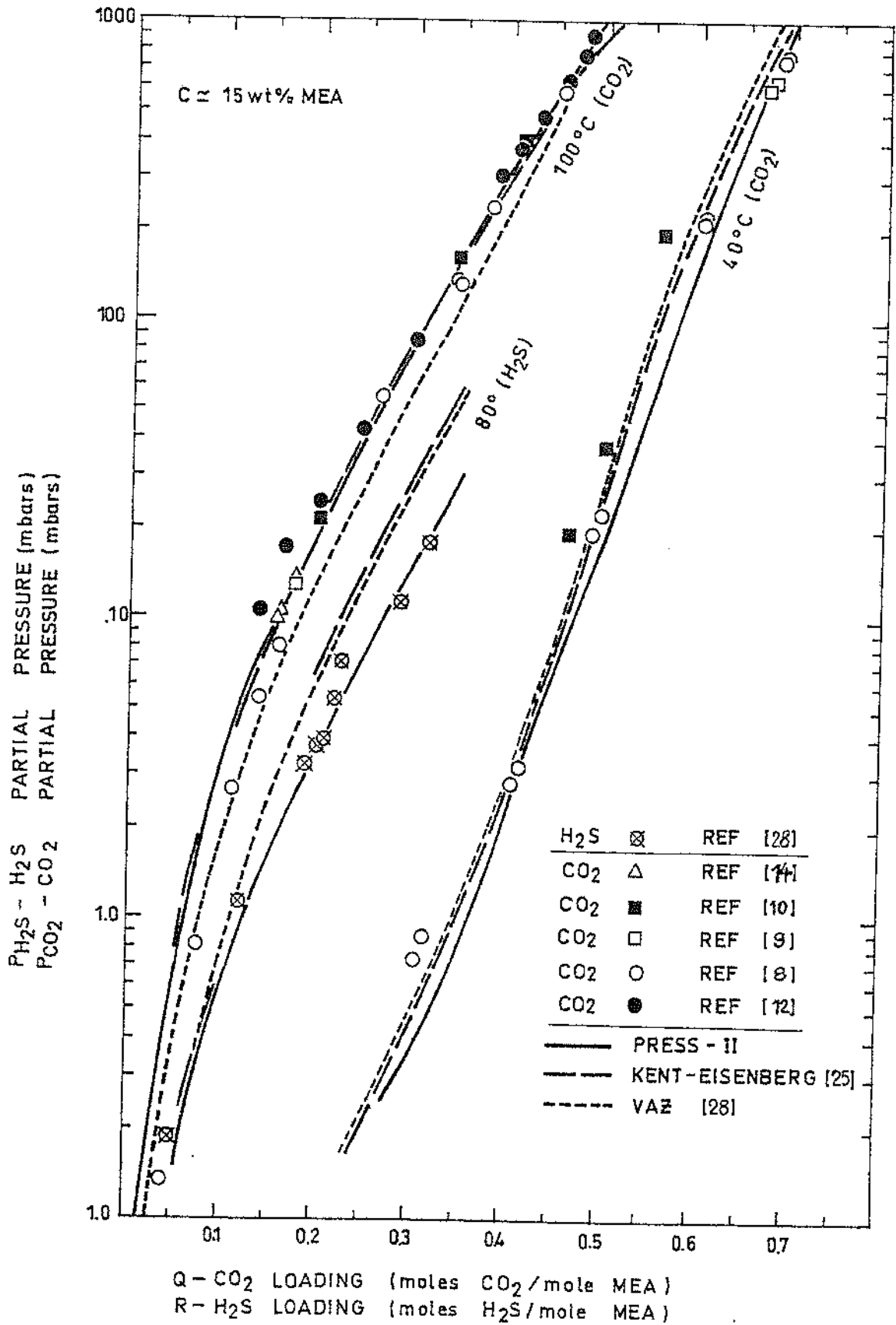


Figure 15 Comparison of the present work with other equilibrium models and experimental data in the systems H_2S or CO_2 -aqueous MEA solution of 15wt% MEA.