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A mathematical model for the simulation of chemical absorption columns

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SEZIONE II
(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *A mathematical model for the simulation of chemical absorption columns.* Nota di GIUSEPPE BIARDI, presentata [*] dal Socio G. NATTA.

RIASSUNTO. — Questa Nota presenta lo sviluppo di un modello matematico concepito per la simulazione delle colonne di purificazione del gas naturale mediante l'assorbimento chimico dei gas acidi contenutivi. In particolare è stato considerato il caso delle unità in cui l'idrogeno solforato e l'anidride carbonica vengono rimosse contemporaneamente con soluzioni di etanolammina.

Nel campo di condizioni chimico–fisiche in cui operano tali unità vi è un accoppiamento piuttosto stretto fra la cinetica delle reazioni chimiche che hanno luogo in seno al liquido e la cinetica del trasferimento di materia fra le fasi. A causa della esotermicità dell'assorbimento anche le condizioni di equilibrio, e quindi le forze motrici, variano sensibilmente lungo la colonna.

Su questi problemi e sulla loro traduzione in termini numerici, in un programma di calcolo automatico, si fissa l'attenzione della Nota: gli esempi di simulazione allegati mostrano i possibili campi di impiego delle colonne stesse e la validità del modello come strumento per l'analisi dei processi.

INTRODUCTION

Many industrial installations are faced with the need to eliminate acid gas components such as H_2S and/or CO_2 from the process streams, both to allow further processing of the purified streams themselves and to recover and dispose, in a profitable way, of the valuable H_2S contained therein.

For the sake of conciseness no general description of such processes will be given here; indeed, I shall just consider the particular, even if extremely important, case of natural gas purification. Anyone wanting a broad and detailed picture of the other processes from an industrial view-point should be directed to the classical reference textbooks [1, 2].

Within the natural gas purification processes attention will be drawn to the absorption columns employing aqueous diethanolamine solutions, a widely used solvent which has proved itself particularly attractive both for its chemical and physical properties. In these columns the physical absorption phenomenon is followed by chemical reactions within the liquid phase, whose overall effect is twofold: on one hand, by consuming the acid species they reduce the liquid phase equilibrium counter-pressure, thus increasing the thermodynamic driving forces; on the other one, their occurrence results in a modification of reactant concentration profiles near the gas-liquid interface, that is, in an enhancement of the mass transfer coefficients.

(*) Nella seduta del 14 novembre 1974.

Both effects, the thermodynamic and the kinetic one, play an important role in determining the overall performance of the absorption columns, where each plate behaves like a gas-liquid reactor.

Even if the absorption in chemical reacting systems is fairly well known from a theoretical view-point and the related phenomena are fully understood (see for instance Ref. [3,4]), there are, however, many difficulties to be overcome in setting up a mathematical model and a computing programme in order to simulate industrial columns.

Such difficulties arise firstly when one is faced with the problem of singling out the proper mass transfer regime among those which are possible a priori.

Moreover a large problem exists in handling and controlling the numerical computations required to solve the set of implicit equations translating the mass and energy balances as well as the continuity relationships between the two phases.

This note deals with the illustration of some of these problems and the way in which they have been solved.

OUTLINES OF THE MATHEMATICAL MODEL

A) *Thermodynamic reactions.*

The stoichiometric and thermodynamic significant chemical reactions are reported in Table I together with an order of magnitude estimate of the related equilibrium constants.

TABLE I

Chemical reactions taking place during H_2S *and* CO_2 *absorption in diethanolamine solutions.*

				Equilibrium constant referred to concentrations (gmole/lt) (range 50°–80° C)
1)	$RNCOO^- + H_2O$	$\rightleftarrows$	$HCO_3^- + RNH$	$O(K1) \simeq 10^{-1}$
2)	H_2S	$\rightleftarrows$	$HS^- + H^+$	$O(K2) \simeq 10^{-7}$
3)	$RNH + H_2O$	$\rightleftarrows$	$RNH_2^+ + OH^-$	$O(K3) \simeq 10^{-5}$
4)	$CO_2 + H_2O$	$\rightleftarrows$	$HCO_3^- + H^+$	$O(K4) \simeq 10^{-7}$
5)	HCO_3^-	$\rightleftarrows$	$H^+ + CO_3^{--}$	$O(K5) \simeq 10^{-11}$
6)	H_2O	$\rightleftarrows$	$H^+ + OH^-$	$O(K6) \simeq 10^{-14}$

It is worthwhile noting that CO_2 absorption results in the formation of three chemical components: the carbamate, the bicarbonate and the carbonate; on the contrary absorbed H_2S reacts giving practically only HS^- ions.

The first problem met was the computation of the equilibrium composition as obtained from assigned temperature and free amine concentration and for given total carbonation and sulphidation ratios

α_{tot} = moles CO_2 into the solution/moles of free RNH;
β_{tot} = moles H_2S into the solution/moles of free RNH.

This demands the satisfying of three independent mass balances (amine, CO_2 and H_2S) and of electrical neutrality coupled with the equilibrium relationships of the six aforementioned reactions.

The formal expressions obtained are summarized in Table II. This nonlinear set of equations was solved by a numerical iterative method, properly conceived to treat such cases, that demands only about 15 iterations to converge towards the solution with a tolerance of 10^{-3} on the relative error of the computed concentration. This method too, embodies the automatic build up of starting guesses, according to the suggestions of Astarita for the similar case of CO_2 absorption in MEA solutions [3].

TABLE II

Equilibrium equations for the reacting mixture obtained during the absorption of CO_2 *and* H_2S *in aqueous DEA.*

Let be

CTA	free amine concentration [gmole/lt]
α_{tot}	carbonation molar ratio [—]
β_{tot}	sulphidation molar ratio [—]

1) Amine balance

$$CTA = [RNH] + [RNH_2^+] + [RNCOO^-]$$

2) CO_2 balance

$$\alpha_{tot} \cdot CTA = [RNCOO^-] + [HCO_3^-] + [CO_3^{--}] + [CO_2]$$

3) H_2S balance

$$\beta_{tot} \cdot CTA = [HS^-] + [H_2S]$$

4) Electrical neutrality

$$[RNH_2^+] + [H^+] = [RNCOO^-] + [HCO_3^-] + [HS^-] + 2 \cdot [CO_3^{--}] + [OH^-]$$

5) Equilibrium requirement for each single chemical reaction

$$K_1 = \frac{[HCO_3^-][RNH]}{[RNCOO^-]} \qquad K_2 = \frac{[HS^-][H^+]}{[H_2S]}$$

$$K_3 = \frac{[RNH_2^+][OH^-]}{[RNH]} \qquad K_4 = \frac{[HCO_3^-][H^+]}{[CO_2]}$$

$$K_5 = \frac{[H^+][CO_3^{--}]}{[HCO_3^-]} \qquad K_6 = [H^+][OH^-]$$

No attempt was made to take into account possible non ideal solution effects in terms of activity coefficients, not to correct the Henry constants of the two gaseous components; it should be noticed, however, that the equilibrium constants, too, were obtained by regression of published or laboratory data following the same assumptions.

A particular care was taken in making the computing procedure insensitive to ill-conditioning related to the rather large range of operating conditions to be considered. For instance at the bottom end of the absorption column the carbonation and sulphidation ratios may be very high and the free amine is present at low concentrations; at the other end when one analyzes the liquid solution up to the top plates the acid component content vanishes ($\alpha_{tot} \rightarrow 0$, $\beta_{tot} \rightarrow 0$) and the mixture becomes more and more basic with an increasing importance of hydroxylic ions $[OH^-]$, otherwise fairly negligible, in establishing the mixture composition.

B) *Kinetic reactions.*

It is accepted throughout the world that reactions consisting of the transfer of a hydrogen ion between two solute molecules or between one solute molecule and the solvent may be considered always in equilibrium conditions, or, in other words, to occur instantaneously [3, 4].

This happens without regard to other possible parallel reactions. Among the elementary reaction steps, by which CO_2 and H_2S are absorbed and react in aqueous DEA all reactions may be assumed to be instantaneous except the following ones:

1) $CO_2 + 2RNH \rightleftarrows RNCOO^- + RNH_2^+$
2) $CO_2 + OH^- \rightleftarrows HCO_3^-$
3) $CO_2 + H_2O \rightleftarrows H^+ + HCO_3^-$.

Table III shows the form of the pertaining reaction rates, together with the values of the involved kinetic constants. A few remarks should be made at this point.

Firstly there is a difference between H_2S and CO_2 as to what concerns their rate of disappearance in the reacting mixture; while the former is always absorbed in the instantaneous reaction regime, i.e. with the maximum possible rate, the latter may be limited by finite kinetic constants, so the global process might be selective in H_2S absorption if proper operating conditions are found. Secondly the total consumption rate of CO_2 is dominated by the reaction 1) forming the carbamate, the other two reactions, resulting in the formation of bicarbonate and carbonate ions, contributing to an extent of less than 1 %.

Thirdly, regardless of the distinction between instantaneous and finite rate reactions, the absolute value of the reaction rates themselves is quite large in comparison with the residence times of the liquid phase on the column plates, the order of magnitude of which is 1 second, so one can fairly assume that the bulk of the liquid mixture is always under equilibrium conditions.

TABLE III

Non instantaneous reactions in CO_2 *absorption in aqueous DEA.*

Reaction	Reaction rate
1) $CO_2 + 2RNH \rightleftarrows RNCOO^- + RNH_2^+$	$R_1 = K_{AM}\left\{[RNH]\,[CO_2] - \frac{[RNH_2^+][RNCOO^-]}{[RNH]\cdot Keq\ 1}\right\}$
2) $CO_2 + OH^- \rightleftarrows HCO_3^-$	$R_2 = K_{OH}\left\{[OH^-]\,[CO_2] - \frac{[HCO_3^-]}{Keq\ 2}\right\}$
3) $CO_2 + H_2O \rightleftarrows H^+ + HCO_3^-$	$R_3 = K_c\left\{[CO_2] - \frac{[H^+]\,[HCO_3^-]}{Keq\ 3]}\right\}$

where

$$K_{AM} \simeq 1.50\times10^3 \exp\left[-4070\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad \frac{lt}{gmole\cdot sec}$$

$$K_{OH} \simeq 8.10\times10^3 \exp\left[-6750\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad \frac{lt}{gmole\cdot sec}$$

$$K_c \simeq 2.54\times10^{-2} \exp\left[-7750\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad sec^{-1}$$

And the equilibrium constants may be evaluated by a combination of the constants defined in Tables I and II.

This means that kinetic effects are restricted to the modification of liquid phase mass transfer coefficient. Therefore the phenomenological analysis was directed towards singling out the proper reaction regime for CO_2, according to the local operating conditions when moving throughout the column, as well as towards the correct computation of the enhancement factors of physical mass transfer coefficients.

From the above kinetic analysis CO_2 chemical absorption may be looked upon as a second order reaction, requiring a coreactant which must diffuse from the bulk fluid.

Accordingly two asymptotic reaction regimes have to be considered [3]; they are:

1) Instantaneous reversible reaction;
2) Pseudo-first order reaction.

Transition from one regime to the other one depends on the conditions prevailing at each plate in the column according to the actual value of Hatta number for CO_2 consuming reactions. This reads:

$$Ha = \frac{\sqrt{K_{tot}\,D_{LCO_2}}}{K_{LCO_2}} \tag{1}$$

where

$K_{tot} = K_{AM}[RNH] + K_{OH}[OH^-] + K_c$;
K_{tot} = Total pseudo 1st order kinetic constant for CO_2 consumption;
D_{LCO_2} = diffusivity of CO_2 in the liquid phase;
K_{LCO_2} = physical mass transfer coefficient for CO_2 in the liquid phase.

All concentrations appearing in the Hatta number must be evaluated at interface conditions, i.e. they still depend on the mass fluxes.

Actually, in order to ease the automatic computational procedure of interphase transfer rates in the absorption column, both the enhancement factors, for the two asymptotic situations, are computed, then the one which shows less value is chosen. This agrees with the general rule that among many concurrent phenomena that which is the slowest is the controlling one.

Table IV reports the expression of net mass flow-rates at the gas-liquid interface for the two aforementioned situations under the general assumptions of 1) equal diffusivities in the liquid phase, and 2) two films theory [3, 4].

TABLE IV

Formal expressions of interfacial mass fluxes.

$$N_{CO_2} = K_{G,CO_2} ([CO_2]^* - [CO_2]_i) = E_{CO_2} K_{L,CO_2} ([CO_2]_i - [CO_2]_b)$$

$$N_{H_2S} = K_{G,H_2S} ([H_2S]^* - [H_2S]_i) = E_{H_2S} K_{L,H_2S} ([H_2S]_i - [H_2S]_b)$$

with

$$E_{H_2S} = \frac{1 + CTA\,(\beta_i - \beta_b)}{[H_2S]_i - [H_2S]_b}$$

$$E_{CO_2} = \begin{cases} E_iCO_2 = 1 + \dfrac{CTA\,(\alpha_i - \alpha_b)}{[CO_2]_i - [CO_2]_b} & \text{if } E_iCO_2 \leq E_1CO_2 \\ E_1CO_2 = Ha/ThHa & \text{if } E_iCO_2 \geq E_1CO_2 \end{cases}$$

where

$K_{G,A}$ = gas–phase mass transfer coefficient for the component A;

$K_{L,A}$ = liquid-phase mass transfer coefficient for the component A;

α = chemical carbonation ratio;

β = chemical sulphidation ratio;

E_A = enhancement factor of liquid phase mass transfer coefficient for the component A

The asterisk (*) refers to concentrations equivalent to gas-phase partial pressures. The index *i* refers to interfacial conditions. The index *b* refers to liquid phase bulk conditions.

It goes without saying, of course, that, irrespective of the actual regime attained, all reactions but the ones considered in the first order reaction scheme reach equilibrium conditions even at the gas-liquid interface.

The gross consequence of such a situation is that the two reaction paths by which CO_2 and H_2S are fixed in the DEA solution always interact between themselves because of the common co-reactants required; that means also, that the presence of each gas inhibits the reaction of the other.

C) *Tray model.*

The simulation program set up envisages the possibility of utilizing both bubble-cap and sieve trays; moreover, because of the modular structure given to it, there is no serious problem in extending its subroutines to cover other plate types. In any case, industrial columns for natural gas purification have fairly large diameters, so provision has been made to account for the liquid phase chemical evolution during its movement on the tray in cross-flow with the rising gas phase.

Actually the plate model built up assumes that the column trays behave like a series of completely stirred mixers each of them being cross-flowed by the gas stream, following the idealized scheme reported in fig. 1.

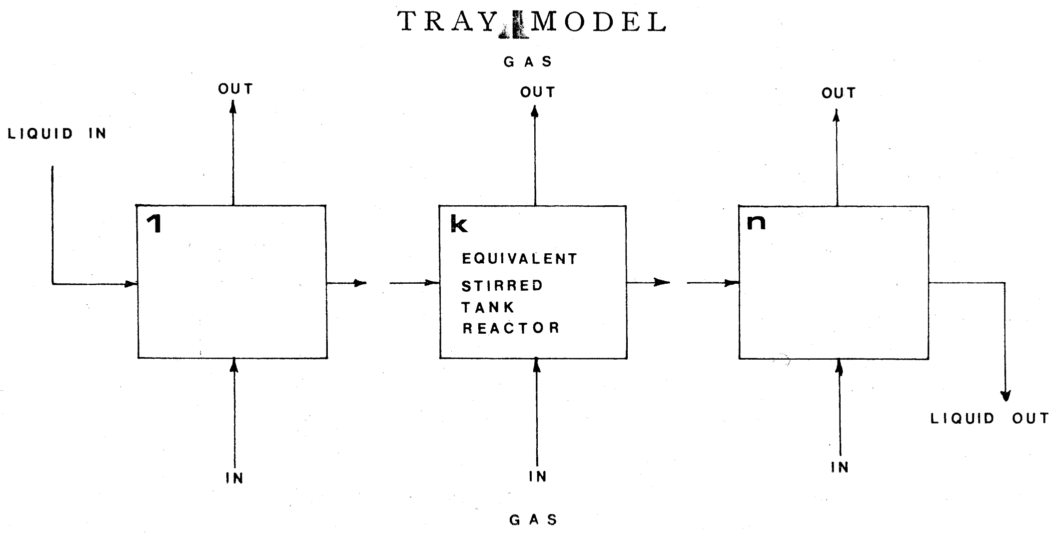

Fig. 1.

Such a lumping procedure on the one hand allows one to solve, without great difficulties, the plates by plate material balances coupled with gas liquid net fluxes under non equilibrium conditions, while on the other hand, it is still possible to account, in a realistic way, for the longitudinal dispersion phenomena on the tray.

As for the relevant parameters related to the tray hydraulics, a few of them were estimated by means of the correlations of " Bubble Tray Design Manual " of AIChE [5]. These are:

- froth height;
- clear liquid height;
- eddy diffusion coefficient for liquid mixing.

Moreover Sharma's correlations [6] were used to evaluate the physical mass transfer coefficients and the specific interfacial area. The lumping criterion adopted, when passing from a distributed parameter description in terms of longitudinal eddy diffusion to the series of equivalent well stirred reactors, may be expressed as follows, according to the Ref. [7].

$$\frac{1}{N_{\text{mixers}}} = \frac{2}{\text{Pe}} - \frac{2}{\text{Pe}^2}\left(1 - e^{-\text{Pe}}\right) \tag{2}$$

$$\text{Pe} = \frac{\langle V \rangle L}{D_E} \tag{3}$$

where the Péclet number is related to the mean liquid velocity ($\langle V \rangle$) and to the effective longitudinal path on the tray (L).

The computational problem at this point consists in solving, for each equivalent mixer of the tray, the set of algebraic or functional equations resulting from the statement of:

– material balances for the two reacting gases;

– continuity equations between the two phases;

– equilibrium conditions for the bulk liquid phase,

– gas-liquid mass transfer rates according to the two schemes previously dealt with.

This set of non linear equations has been solved with a properly conceived numerical method whose features may be summarized as follows:

– it behaves like an interative method, with an automatically computed starting point and with the introduction of convergence promoters to ensure a steady and quick approach to the solution (see for details [8]);

– inside the global computing loop, however, the resolution of the continuity equations between the two phases in terms of interfacial composition variables, has been obtained by applying a modified Newton method for non linear equations.

Together with material balances the enthalpy balance has also been introduced in plate by plate calculations, because of the large dissolution heats associated with the absorption of acid gases in aqueous DEA and, hence, of the important temperature differences to be expected between adjacent trays. Gas and liquid phase temperatures were, however, taken as average values on the tray, to avoid eccessive computing times. Such computation, performed after the solution of the tray material balances, presented no additional problems besides the one of providing the program with the necessary thermochemical data.

D) *Column model.*

The column model is, simply, the coordinate gathering of the tray model with the information at one's disposal for the simulation problem at hand, i.e. the actual states of the streams entering into the column.

This problem is, by its structure, *a two point boundary condition problem*, which cannot be solved by any marching numerical procedure. There is therefore, a need to developing an overall iterative computation, starting with a guess of the liquid output stream and passing through successive modifications of it till the estimated liquid input stream on the top side of the column matches the assigned values.

Such an iterative computation loop, too, has been accelerated by means of convergence promoters developed on physical grounds; in any case, due to the very small quantities of acid gases escaping from the top of actual industrial columns (order of magnitude 50 p.p.m), the simulation problem demands only 3 or 4 global iterations.

STRUCTURE OF THE PROGRAM

The structure given to the program is quite simple. The MAIN program accomplishes the task of acquiring the simulation data by means of READ cards; the data concern both the column geometric parameters and the state and operating variables of gas and liquid feeds.

After that the MAIN program undertakes to organize the logical and numerical resolution of the column model, by performing computations by itself or by calling ancillary subroutines, particularly devoted to specific and definite tasks. These are:

SUBROUTINE EQUIL	which implements the method chosen for equilibrium computations;
SUBROUTINE ZERO	to find the root of algebraic or transcendental equations of one unknown by the half-interval method;
SUBROUTINE PROP	to estimate the physical properties of both components and mixtures to be utilized by the mathemathical model;
SUBROUTINE ZEZ	to build up the functions $F(x)$ where roots are to be found by SUBROUTINE ZERO;
FUNCTION EQC	to compute equilibrium constants for the chemical reactions occurring as well as Henry's constants, as functions of absolute temperature.

Occupation of memory is about 12,000 decimal words and the computing time (C.P.U. computing time) has an order of magnitude of 20 seconds on a 1108 UNIVAC machine.

SIMULATION CASES AND DISCUSSION

Many simulation runs have been made by means of the computing program set up and described in its main features in the previous paragraphs.

Investigated cases concerned existing industrial columns with the aim of the check of the validity of the program itself and in order to study the effect of modifying the conditions at the operator's disposal.

Moreover a thorough analysis has been made in order to single out a range of operating conditions where the chemical absorption process might be selective in H_2S absorption. In these cases the final aim was to provide oneself with pieces of information for the possible development of a process to upgrade low concentration H_2S streams for chemical purposes. Two simulation examples of both kinds are here presented.

Example 1. High pressure absorption.

This example refers to an absorption column in operation for natural gas purification.

Geometrical details are synthetized as follows:

column diameter 2.434 mm;
20 bubble cap trays with a split flow arrangement;
tray spacing 0.60 m.

Operating conditions are:

gas-flow rate 2.151 Mm^3/day;
DEA flow rate 407 m^3/h;

Free amine concentration	2.88	gmole/lt
H_2S molar fraction at the inlet	0.098	—
CO_2 molar fraction at the inlet	0.147	
Gas temperature at the inlet	36° C	—
Liquid temperature at the inlet	67 °C	
Average pressure in the column	75.5	bar (gauge).

Computations results are summarized in figg. 2 and 3 and in Tables V and VI. From fig. 2 one can get an idea of the heat effects associated with the reactions in the liquid phase.

The largest temperature differences between contiguous trays are located from the 7th to the 11th trays in the column, starting from the bottom end, as shown by the presence of an inflexion point in liquid temperature profile.

Correspondingly there is a sharp modification of the derivative of gas molar fraction profiles for CO_2 and H_2S in the semi-log plot (fig. 3 with the index N).

In fact, under the seen operating conditions, at these plates there is the transition between the two mass transfer regimes in the liquid phase previously dealt with.

As a consequence two zones of the column may be defined: the lower one where instantaneous reactions occur for both gases, even if with relatively small enhancement factors because of the low free amine content, and the upper one where H_2S always reacts instantaneously with ever increasing rate until gas phase mass transfer coefficient becomes rate controlling, whilst CO_2 absorption is partially limited by its reaction rate with the free amine. The gross result, however, is an almost complete purification of the natural gas.

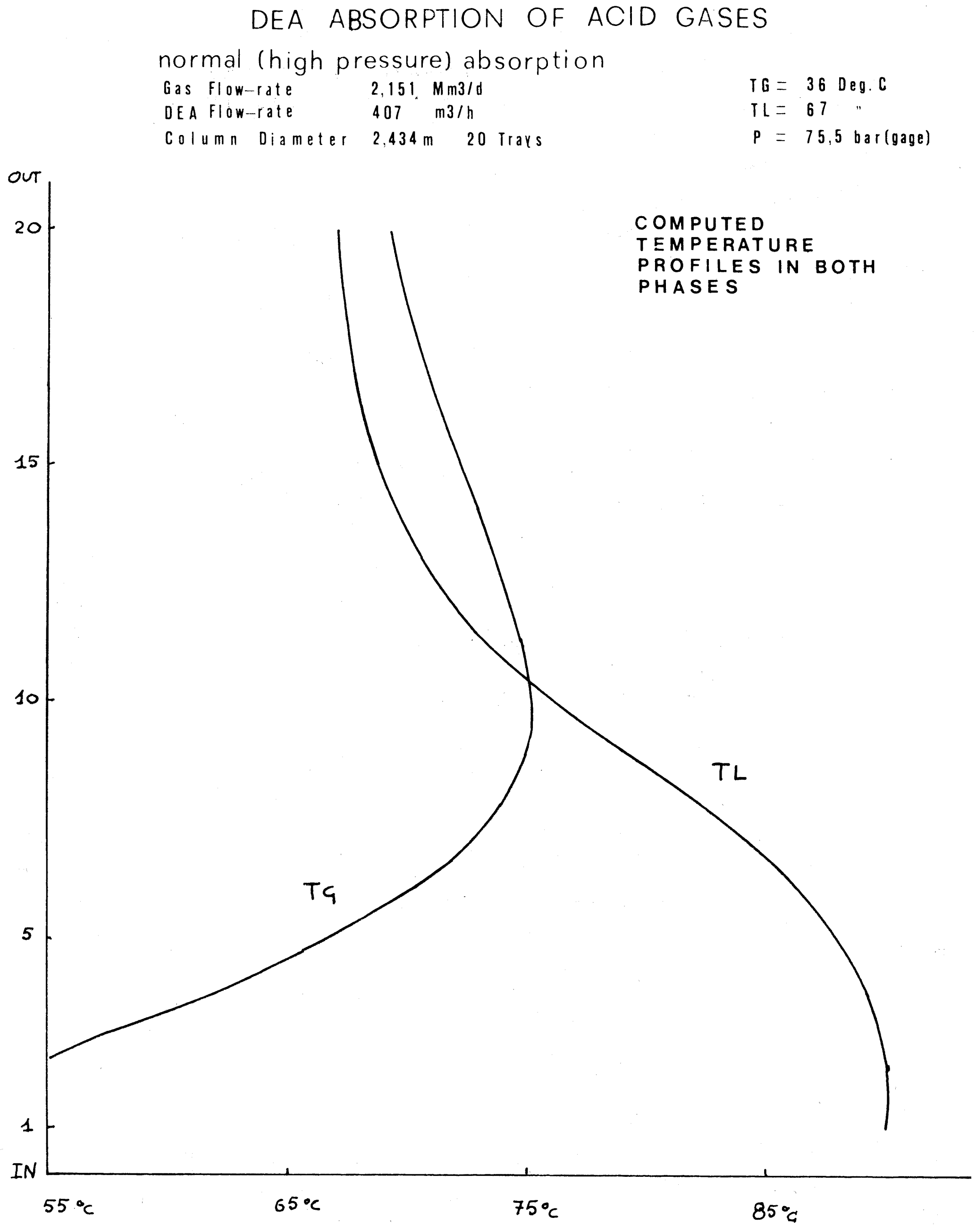
DEA ABSORPTION OF ACID GASES
normal (high pressure) absorption
Gas Flow-rate 2,151 Mm3/d
DEA Flow-rate 407 m3/h
Column Diameter 2,434 m 20 Trays
TG = 36 Deg. C
TL = 67 "
P = 75,5 bar(gage)
COMPUTED TEMPERATURE PROFILES IN BOTH PHASES
OUT
20
15
10
5
1
IN
TL
Tg
55 °c
65 °c
75 °c
85 °c

Fig. 2.

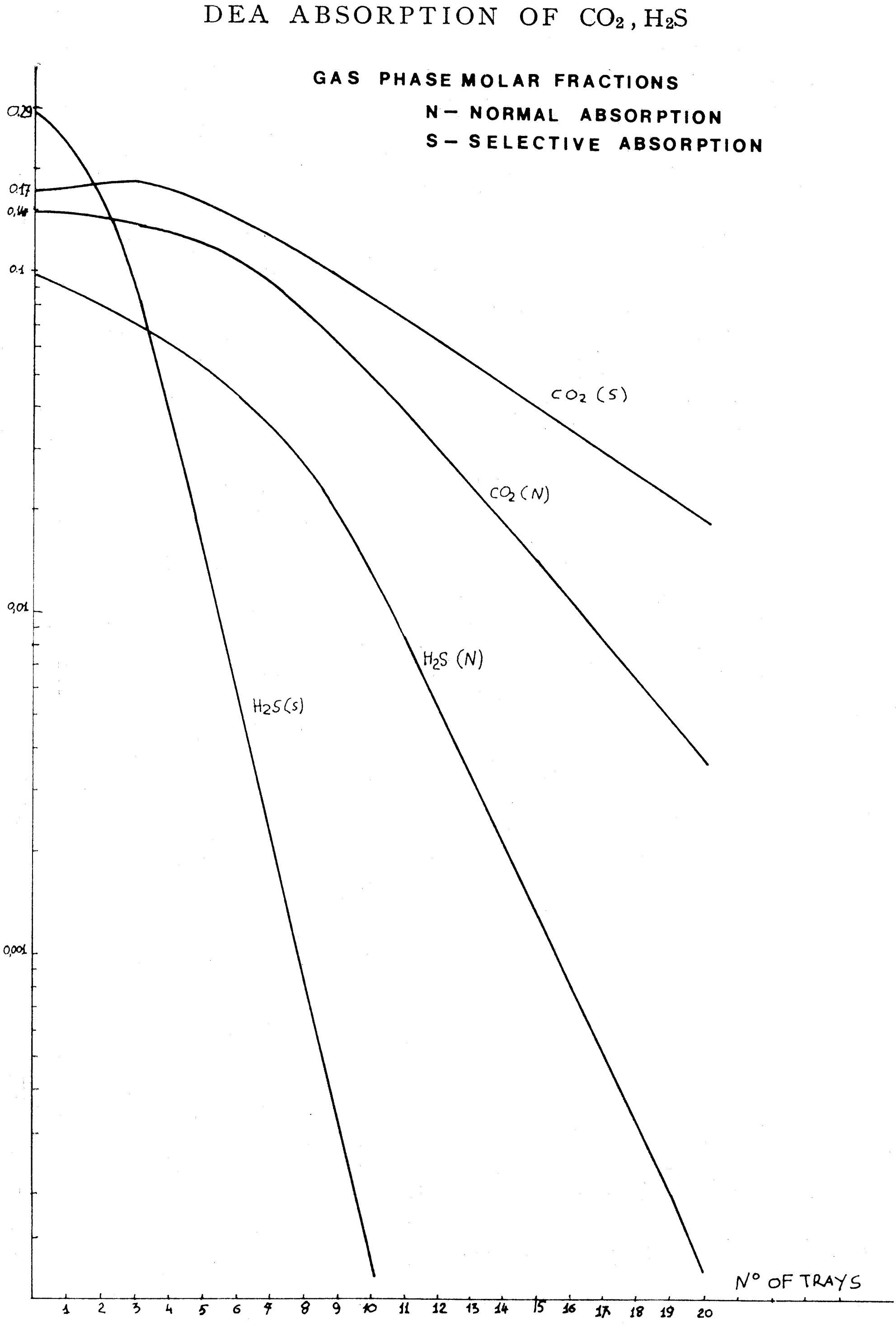
DEA ABSORPTION OF CO_2, H_2S

Fig. 3.

Table V shows for one tray the main parameters concerning the tray hydraulics and purely physical mass transfer; it should be noticed that these parameters, here reported for a specific tray, are slowly varying throughout the column.

TABLE V

Tray hydraulics and transfer parameters for high pressure absorption (Example N. 1).

The following conditions refer to the 1st tray from the bottom

froth height = 43.1 cm

clear liquid height = 11.8 cm

submergence = 37.1 cm

Pé number = 11.7

Number of equivalent stirred reactors = 6

specific area = 0.85 cm^2/cm^3

gas-phase mass transfer coefficient for H_2S = 0.141 cm/sec (referred to liquid phase equivalent concentrations)

gas-phase mass transfer coefficient for CO_2 = 0.501 cm/sec (referred to liquid phase equivalent concentrations)

liquid-phase mass transfer coefficient for H_2S = 1.97×10^{-2} cm/sec

liquid-phase mass transfer coefficient for CO_2 = 2.18×10^{-2} cm/sec

On the contrary the bulk liquid phase composition, as reported in Table VI, shows the most rapid variations when passing from the first equivalent completely stirred reactor on the first plate to the last one on the top of the column. The history of enhancement factors for CO_2 and H_2S is heavily dependent on such variations of liquid mixture composition.

Example 2. Low pressure, low temperature absorption.

In order to take advantage of the differences existing between CO_2 and H_2S as for their physico-chemical properties and behaviour during absorption in aqueous DEA, there is the need to create an environment where CO_2 absorption is depressed while H_2S absorption has to be enhanced, the reverse case being almost impossible to achieve. Both requirements are met when operating at reduced absolute pressures and at temperature levels that are lower than the usual ones, as shown, for the simulation run here reported, by figs. 3 (index S) and 4.

TABLE VI. – *Liquid phase bulk composition for high pressure absorption* (Example N. 1).

1st stirred reactor of the
1st tray (from the bottom side)
Instantaneous reaction regime

```
T= 90.00   TOTAL AMINE CONCENTRATION=  2.88
ALTOT= 4.708-01   BETOT= 3.130-01
ALFA=  4.572-01   BETA=  2.946-01
KZER=  10   1.000-03
CRNH=  4.924-01   PCO2=  3.435+00   PH2S=  1.328+00   CCO2=  3.954-02   CH2S=  5.342-02
RNH2+=  .2172196+01   RHCOO-=  .219913+00   HCO3-=  .10952557+01   CO3--=  .3560081-02
HS-=  .8497597+00   OH-=  .1449744-04   H+=  .2624889-07

HAB=  .2345570+02   AKTOT=  .8510128+04   SEC-1   TAU=  .5245961-00   SEC
ECO2=  .1545002+01   EH2S=  .3340211+01
```

1st stirred reactor of the
9th tray
Transition reaction regime

```
T= 78.95   TOTAL AMINE CONCENTRATION=  2.88
ALTOT= 1.869-01   BETOT= 7.238-02
ALFA=  1.867-01   BETA=  7.202-02
KZER=  10   1.000-03
CRNH=  1.847+00   PCO2=  4.487-02   PH2S=  2.378-02   CCO2=  5.737-04   CH2S=  1.045-03
RNH2+=  .7586560+00   RNCOO-=  .2785198+00   HCO3-=  .2473590+00   CO3--=  .1232975-01
HS-=  .2077468+00   OH-=  .1441219-03   H+=  .1655616-08

HAB=  .3810974+02   AKTOT=  .2247550+05   SEC-1   TAU=  .5347277+00   SEC
ECO2=  .3362703+02   EH2S=  .8149852+02
```

6th stirred reactor of the
20th tray
1st order reaction regime

```
T= 67.11   TOTAL AMINE CONCENTRATION=  2.88
ALTOT= 8.559-03   BETOT= 6.401-03
ALFA=  8.559-03   BETA=  6.401-03
KZER=  11   1.000-03
CRNH=  2.818+00   PCO2=  1.965-05   PH2S=  6.300-05   CCO2=  2.898-07   CH2S=  3.127-08
RNH2+=  .5373212-01   RNCOO-=  .1267438-01   HCO3-=  .4664384-02   CO3--=  .7351554-02
HS-=  .1846459-01   OH-=  .3225660-02   H+=  .4246357-10

HAB=  .3948155+02   AKTOT=  .2332395+05   SEC-1   TAU=  .5420200+00   SEC
ECO2=  .3939028+02   EH2S=  .2364124+04
```

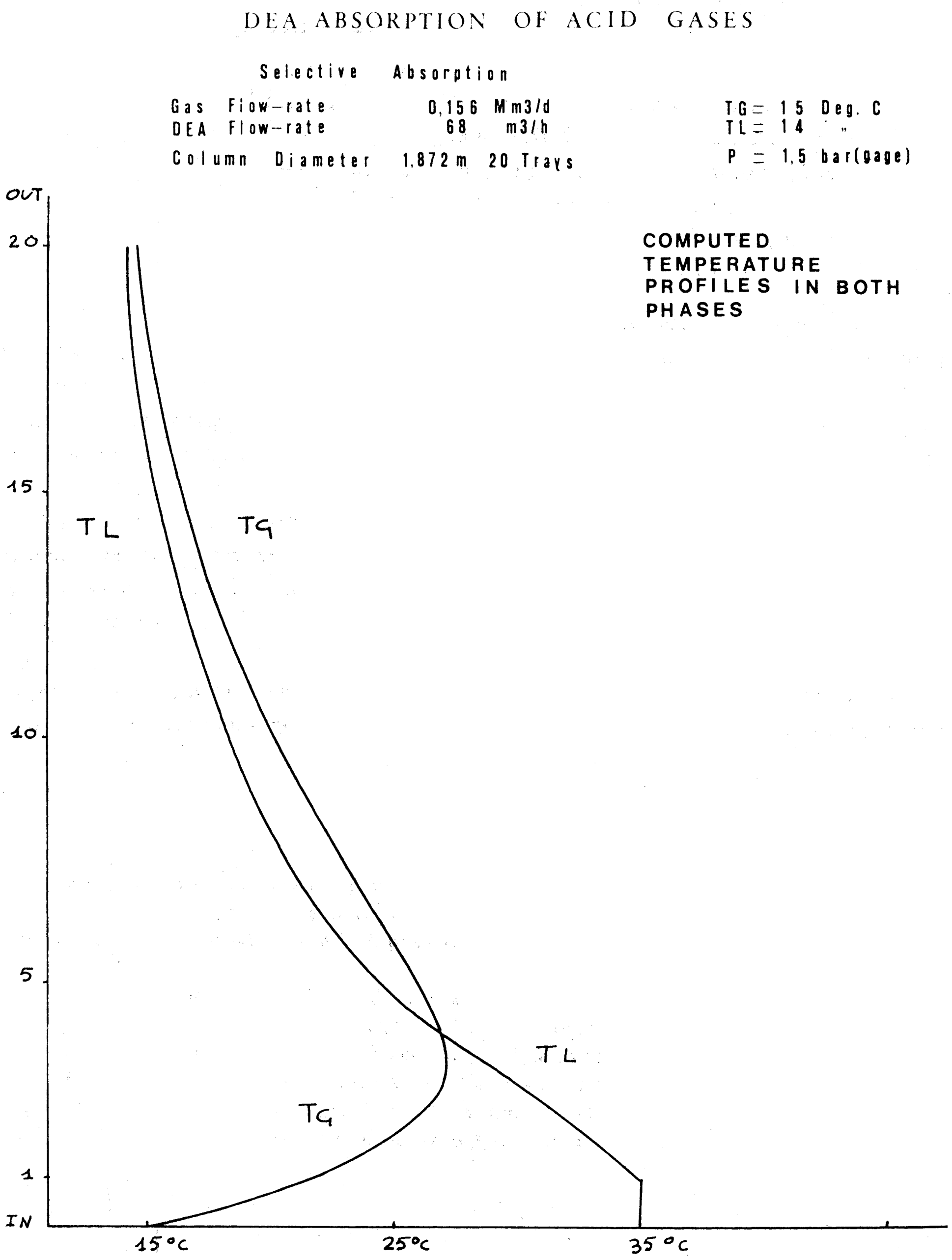

Fig. 4.

In this case the geometric details of the column are:

column diameter	1.872 m
20 single cross flow bubble cap trays	
tray spacing	0.600 m

Operating conditions are:

gas flow rate	0.156	Mm^3/day
DEA flow rate	68.0	m^3/h
free amine concentration	3.14	gmole/lt
H_2S molar fraction at the inlet	0.290	—
CO_2 molar fraction at the inlet	0.132	—
gas temperature at the inlet	15 °C	
liquid temperature at the inlet	15 °C	
average pressure in the column	1.5 bar (gauge)	

Fig. 3 clearly puts one against the other the gas phase molar fraction profiles af CO_2 and H_2S for the two simulated cases. It is quite apparent that a great difference exists; as a matter of fact, as for the low pressure column, CO_2 absorption is always in the pseudo-first order reaction regime and, because of the reduced temperature level, with a correspondingly reduced kinetic constant.

On the contrary H_2S absorption does not suffer from these kinetic restrictions, yet at low temperature the thermodynamics driving forces become greater and the only withstanding effect is gas-phase diffusions towards the interface. Temperature profiles are reported in fig. 4. The net result of such a situation is that the absorption process may be locally, and also globally, a very selective one, thus confirming the possibility of obtaining, after regeneration, a H_2S rich gas stream suitable directly for chemical purposes.

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