Simultaneous Mass Transfer of H₂S and CO₂ with Complex Chemical Reactions in an Aqueous Di-isopropanolamine Solution

Gleichzeitige Absorption von H₂S und CO₂ in Wässriger Di-isopropanolaminlösung

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Abstract

The absorption of H₂S and CO₂ into an aqueous di-isopropanolamine (DIPA) solution was studied experimentally and theoretically as an example of simultaneous mass transfer with complex reversible reactions.

The absorption phenomena were classified into three regimes: (1) negligible mutual interaction between the CO₂ and H₂S absorption, (2) intermediate interaction, and (3) extreme interaction leading to forced desorption of one of the gaseous components, while based on its overall driving force absorption would be expected. The key parameter largely determining the transitions between these regimes is the extent of depletion of the alkanolamine in the penetration zone.

In order to study these phenomena, simultaneous absorption experiments were carried out in each of the three regimes mentioned above using a stirred cell reactor and for some experiments a wetted wall column.

The experimental results were evaluated by means of a numerical solution of the penetration model description of simultaneous mass transfer with complex reactions (Cornelisse *et al.*, *Chem. Eng. Sci.*, 35 (1980) 1245). Recently we derived a numerical film theory description, which has also been incorporated in the evaluation. The measured hydrogen sulphide fluxes fall between film and penetration theory calculations, whereas the CO₂ fluxes are closer to the film theory.

Kurzfassung

Die Absorption von H₂S und CO₂ in wässrigen Di-isopropanolaminlösungen (DIPA) wurde experimentell und theoretisch untersucht. Es handelt sich hierbei um einen Vorgang, der durch die Kopplung von Stoffübertragung mit chemischen Reaktionen gekennzeichnet ist.

Der Absorptionsvorgang wurde in drei Bereiche unterteilt: (1) Vernachlässigbare, gegenseitige Wechselwirkung zwischen CO₂ und H₂S Absorption; (2) mässige Wechselwirkungen; (3) ausserordentlich starke Wechselwirkungen zwischen diesen beiden Gasen.

Im letzteren Fall wurde eine erzwungene Desorption einer der beiden Gaskomponenten beobachtet, obwohl man aufgrund des globalen Konzentrationsgefälles Absorption erwartet hätte. Die Schlüsselgrösse, die die Übergänge zwischen den drei Gebieten steuert, ist das Ausmass der Verarmung der Penetrationszone an Alkanolamine.

Die gleichzeitige Absorption von CO₂ und H₂S wurde in einem Rührkesselreaktor wie auch in einer Fallfilmkolonne experimentell in allen drei obengenannten Bereichen untersucht.

Die Versuchsergebnisse wurden verglichen mit einer numerischen Lösung des Penetrationsmodelles, das in Cornelisse *et al.* (*Chem. Eng. Sci.*, 35 (1980) 1245), für die simultane Absorption mit chemischer Reaktion entwickelt wurde. Ausserdem wurde auch die Filmtheorie zum Vergleich herangezogen. Die gemessenen H₂S-Absorptionsgeschwindigkeiten liegen zwischen den Ergebnissen der Film- und der Penetrationstheorie, wohingegen die CO₂-Absorptionsgeschwindigkeit näher bei den Ergebnissen der Filmtheorie liegt.

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Synopse

Gleichzeitiger Stoffaustausch von mehreren Komponenten zwischen einer Gasphase und einer Flüssigkeit kommt in der Praxis sehr häufig vor. Eine der wichtigsten industriellen Anwendungen bei der dieser gleichzeitige Stoffaustausch eine grosse Rolle spielt, ist die Absorption von Schwefelwasserstoff und Kohlendioxid mit Alkanolamin in wässrigen Lösungen um z.B. (Erd)Gas zu entschwefeln. Es ist von grossem wirtschaftlichen Interesse, diesen Prozess gründlich zu verstehen, um ihn dadurch verbessern zu können. Insbesondere ist eine Erhöhung der Selektivität für die Absorption von Schwefelwasserstoff energetisch und deshalb wirtschaftlich sehr attraktiv.

In unserem Labor haben wir daher diesen Absorptionsprozess experimentell sowie theoretisch untersucht. Neben dem Stoffaustausch zwischen Gasphase und Flüssigkeit sind die in der Flüssigkeit auftretenden Diffusionsprozesse mit gleichzeitiger und interaktiver Reaktion besonders komplex (Gl. (1), (3)–(5), (8)–(22)) und bestimmen die Stoffaustauschphänomene an der Grenzfläche.

Im Allgemeinen kann man diese Phänomene in drei Bereiche einteilen. In jedem Bereich wurden Experimente ausgeführt mit Hilfe sogenannter Modelreaktoren.

Im ersten Bereich sind die Gasphasenkonzentrationen von H_2S und CO_2 relativ niedrig und deshalb ist der kombinierte $H_2S + CO_2$ Molenstrom niedrig. Der Flüssigkeitsreaktant, Alkanolamin, kann in diesem Fall genügend schnell von der Hauptmasse in die Reaktionszone zugeführt werden, und das gemeinsame Produkt, protoniertes Amin, von der Reaktionszone in die Hauptmasse abgeführt werden. Die Stoffaustauschgeschwindigkeiten von H_2S und CO_2 sind in diesem Fall nahezu unabhängig voneinander und können mit analytischen Lösungen von relativ einfachen Stoffaustausch-(differential)-gleichungen beschrieben werden. Die Selektivität des gleichzeitigen Absorptionsprozess, definiert als das Verhältnis der H_2S Absorptionsgeschwindigkeit und der gesamten ($H_2S + CO_2$) Absorptionsgeschwindigkeit, ist in diesem Gebiet proportional zum Gasphasenstoffaustauschkoeffizienten (Fig. 9). Die Übereinstimmung zwischen Experimenten im Fallfilmreaktor (Fig. 4) und im gerührten Reaktor (Fig. 3) und der Theorie ist gut.

Den zweiten Bereich erreicht man bei relativ hohen Gasphasenkonzentrationen von H_2S und CO_2 . Durch die inhärent hohen Absorptionsgeschwindigkeiten von H_2S und CO_2 und eine deshalb hohe totale Reaktionsgeschwindigkeit mit Alkanolamin, entsteht ein Amindefizit und ein protonierter Amin-Überschuss nahe der Grenzfläche. Deshalb hindern H_2S und CO_2 einander bei der jeweiligen Reaktionen mit Alkanolamin, und die jeweiligen Absorptionsgeschwindigkeiten sinken im Vergleich zur Einzelabsorption einer der Komponenten und zum ersten Bereich. Mit zunehmenden Gasphasenkonzentration einer der Komponenten sinkt die Absorptionsgeschwindigkeit der andern Komponente (Fig. 10–13). Die Selektivität liegt erheblich unter den Resultaten im ersten Bereich und erweist sich als Funktion der Stoffaustauschkoeffizienten.

Die mathematische Beschreibung des gleichzeitigen Absorptionsprozesses nach der Filmtheorie und Higbie's Penetrationstheorie (Gl. (8)–(22)) ist sehr komplex, und die relevanten Gleichungen können nur noch mit numerischer Arithmetik gelöst werden (8). Die mathematischen Modelle und die experimentellen Resultate stimmen gut überein, obwohl die gemessene Absorptionsgeschwindigkeiten von CO_2 auf der gleichen Linie liegen mit dem Filmmodell, während H_2S zwischen beide Modelle fällt.

Im dritten Bereich ist eine extrem starke Wechselwirkung vorhanden. Die Absorptionsgeschwindigkeit einer der Gasphasekomponenten ist so hoch, dass das jeweilige Gleichgewicht (Gl. (1) oder (5)) ganz nach rechts gezwungen wird und deshalb ein Alkanolamin-Defizit und ein Überschuss von protoniertem Amin in der Reaktionszone entsteht. Das Defizit kann mittels Diffusion von Alkanolamin aus der Hauptmasse ergänzt werden. Wenn die Diffusion alleine nicht genügt, verlegt das konkurrierende Gleichgewicht sich nach links und produziert lokal Alkanolamin und freies H_2S b.z.w. CO_2 . Die lokale Konzentration kann die jeweiligen Gasphasenkonzentration überschreiten und dann Desorption induzieren. Mit einer speziellen experimentellen Anlage (Fig. 7) haben wir bewiesen, dass diese Phänomene in der Praxis tatsächlich auftreten. Diese sogenannte 'erzwungene' Desorption (gegen eine Konzentrationsdifferenz) kann nur mit unseren mathematischen Modellen beschrieben werden. Die quantitative Übereinstimmung zwischen Experimenten und Modellen im erzwungenem Desorptionsbereich ist befriedigend.

Introduction

Removal of acid components from gases containing H_2S and CO_2 by alkanolamines in aqueous or mixed solutions has become a well-established process during the last decades and will gain even more importance in the near future [1]. Calculation of simultaneous mass transfer of H_2S and CO_2 in these processes, however, has to take into account reversible and, moreover, interacting non-elementary liquid phase reactions [2].

The reaction of H_2S with alkanolamines is known to be reversible and fast with respect to mass transfer [2, 3], while CO_2 also reacts reversibly, but with a slower rate [2, 3].

Several (approximate) analytical solutions are available in the literature for the calculation of the mass transfer flux of a single gas component with reversible [4–7], instantaneous reversible [8, 9] and irreversible liquid phase reaction of finite rate [5, 10–14], or mass transfer fluxes of two gas components with two irreversible reactions [7, 15–19]. None of these analytical solutions, nor combination of solutions, is able, however, to describe the simultaneous mass transfer of H_2S and CO_2 with interacting liquid phase reactions under all conditions [20].

Recently, therefore, we developed a more complete description of the mass transfer and reaction phenomena, taking reversibility of the two reactions into account, and solved the model equations by a three-point backward finite difference method [20]. In this previous

work we showed the stability of the solution method, as well as the agreement between the analytical equations tested and the corresponding limiting cases of our model.

Also recently, Cornelissen [21] published a numerical model based on the film theory, neglecting, however, the reversibility of the CO_2 -alkanolamine reaction.

In the present investigation we carried out experiments with simultaneous absorption of H_2S and CO_2 into aqueous ~ 2.0 M di-isopropanolamine solutions and evaluated the results by means of our mathematical models [20]. The experiments can be classified into three regimes:

- (1) negligible mutual interaction between the H_2S and CO_2 absorptions, realized at relatively low gas phase concentrations,
- (2) with intermediate interaction (at high gas phase concentrations), and
- (3) with extreme interaction, leading to forced desorption [20] of one of the gaseous components.

Under the conditions prevailing in industrial and laboratory absorbers operating at steady state, only the first two regimes can be attained. The third regime probably can be realized only under transient operating conditions, but provides an extremely severe condition for testing the mass transfer models.

The following theoretical considerations will be limited to reactions with primary and secondary alkanolamines.

Theoretical

The liquid phase reactions

The reaction between H_2S and aqueous alkanolamines involves only a proton transfer and can, therefore, be regarded as reversible and 'instantaneously' fast with respect to mass transfer [2, 3]:

with

$$K_{\text{H}_2\text{S}} = \frac{[\text{HS}^-][\text{R}_2\text{NH}_2^+]}{[\text{H}_2\text{S}][\text{R}_2\text{NH}]} \quad (2)$$

Everywhere in the liquid phase, equilibrium (1) is established due to forward and backward reaction rates, which are sufficiently fast with respect to the rates of mass transfer.

CO_2 reacts reversibly with primary and secondary alkanolamines by the reaction equations [2, 3]

with

$$K_{\text{CO}_2} = \frac{[\text{R}_2\text{NCOO}^-][\text{R}_2\text{NH}_2^+]}{[\text{CO}_2][\text{R}_2\text{NH}]^2} \quad (6)$$

Reaction (5) proceeds at a net overall reaction rate according to [3]

$$r = k_2 \left\{ [\text{CO}_2][\text{R}_2\text{NH}] - \frac{1}{K_{\text{CO}_2}} \frac{[\text{R}_2\text{NCOO}^-][\text{R}_2\text{NH}_2^+]}{[\text{R}_2\text{NH}]} \right\} \quad (7)$$

Equations (3)–(5) are, in fact, simplifications of the actual reaction scheme [22, 23] and consequently more complicated rate expressions are suggested in the literature [23]. Also our recent findings suggest a somewhat different rate equation [24]. However, eqn. (7) was found to be sufficiently accurate for the purpose of this work.

Other CO_2 consuming reactions, as well as the hydrolysis of the carbamate ion, R_2NCOO^- , are slow compared with reaction (5) and do not affect the absorption rate significantly. Hence these reactions have not been incorporated in the model.

The mass transfer model

In our previous work [20] the model for simultaneous absorption of H_2S and CO_2 with interactions was described extensively. Here we confine ourselves to a recapitulation of the starting points.

The gas phase mass transfer is described by the stagnant film model, while for the liquid phase Higbie's penetration model is used.

The process of diffusion of the gaseous components and simultaneous reactions in the liquid phase penetration zone is schematically given in Fig. 1 and is expressed by the following combined balance and rate equations [20]:

the partial carbon dioxide accumulation:

$$\begin{aligned} \frac{\partial [\text{CO}_2]}{\partial t} = D_{\text{CO}_2} \frac{\partial^2 [\text{CO}_2]}{\partial x^2} - k_2 [\text{CO}_2][\text{R}_2\text{NH}] \\ + \frac{k_2}{K_{\text{CO}_2}} \frac{[\text{R}_2\text{NCOO}^-][\text{R}_2\text{NH}_2^+]}{[\text{R}_2\text{NH}]} \end{aligned} \quad (8)$$

the total carbon dioxide accumulation:

$$\begin{aligned} \frac{\partial [\text{CO}_2]}{\partial t} + \frac{\partial [\text{R}_2\text{NCOO}^-]}{\partial t} \\ = D_{\text{CO}_2} \frac{\partial^2 [\text{CO}_2]}{\partial x^2} + D_{\text{R}_2\text{NCOO}^-} \frac{\partial^2 [\text{R}_2\text{NCOO}^-]}{\partial x^2} \end{aligned} \quad (9)$$

the total sulphur accumulation:

$$\frac{\partial [\text{H}_2\text{S}]}{\partial t} + \frac{\partial [\text{HS}^-]}{\partial t} = D_{\text{H}_2\text{S}} \frac{\partial^2 [\text{H}_2\text{S}]}{\partial x^2} + D_{\text{HS}^-} \frac{\partial^2 [\text{HS}^-]}{\partial x^2} \quad (10)$$

the total amine accumulation:

$$\begin{aligned} \frac{\partial [\text{R}_2\text{NH}]}{\partial t} + \frac{\partial [\text{R}_2\text{NH}_2^+]}{\partial t} + \frac{\partial [\text{R}_2\text{NCOO}^-]}{\partial t} \\ = D_{\text{R}_2\text{NH}} \frac{\partial^2 [\text{R}_2\text{NH}]}{\partial x^2} + D_{\text{R}_2\text{NH}_2^+} \frac{\partial^2 [\text{R}_2\text{NH}_2^+]}{\partial x^2} \\ + D_{\text{R}_2\text{NCOO}^-} \frac{\partial^2 [\text{R}_2\text{NCOO}^-]}{\partial x^2} \end{aligned} \quad (11)$$

and the acid accumulation:

$$\begin{aligned} \frac{\partial [\text{H}_2\text{S}]}{\partial t} + \frac{\partial [\text{CO}_2]}{\partial t} + \frac{\partial [\text{R}_2\text{NH}_2^+]}{\partial t} \\ = D_{\text{H}_2\text{S}} \frac{\partial^2 [\text{H}_2\text{S}]}{\partial x^2} + D_{\text{CO}_2} \frac{\partial^2 [\text{CO}_2]}{\partial x^2} \\ + D_{\text{R}_2\text{NH}_2^+} \frac{\partial^2 [\text{R}_2\text{NH}_2^+]}{\partial x^2} \end{aligned} \quad (12)$$

At $t \leq 0$, $x \geq 0$ and $t > 0$, $x = \infty$, the liquid is assumed to be in equilibrium with a given carbon dioxide and hydrogen sulphide loading. The combined initial and boundary conditions are expressed by:

$$[\text{CO}_2] + [\text{R}_2\text{NCOO}^-] = \alpha_{\text{CO}_2} [\text{Amtot}] \quad (13)$$

$$[\text{H}_2\text{S}] + [\text{HS}^-] = \alpha_{\text{H}_2\text{S}} [\text{Amtot}] \quad (14)$$

$$[\text{R}_2\text{NH}] + [\text{R}_2\text{NH}_2^+] + [\text{R}_2\text{NCOO}^-] = [\text{Amtot}] \quad (15)$$

$$K_{\text{H}_2\text{S}} = [\text{HS}^-][\text{R}_2\text{NH}_2^+]/[\text{H}_2\text{S}][\text{R}_2\text{NH}] \quad (2)$$

$$K_{\text{CO}_2} = [\text{R}_2\text{NCOO}^-][\text{R}_2\text{NH}_2^+]/[\text{CO}_2][\text{R}_2\text{NH}]^2 \quad (6)$$

and

$$[\text{R}_2\text{NCOO}^-] + [\text{HS}^-] + [\text{HCO}_3^-] = [\text{R}_2\text{NH}_2^+] \quad (16)$$

Equations (13)–(15) represent the initial loadings of the liquid and eqns. (2) and (6) express equilibria for reactions (1) and (5) respectively at $t = 0$ and at infinite depth. Equation (16) is the electrical charge balance. A correction term, $[\text{HCO}_3^-]$, is included in this equation to compensate for the effect of the reaction

on the equilibria. More details are given in ref. 20.

Additional boundary conditions for $x = 0$ and $t \geq 0$ are:

$$\begin{aligned} k_{\text{g}(\text{CO}_2)} \left\{ [\text{CO}_2]_{\text{g}}^0 - \frac{[\text{CO}_2]}{m_{\text{CO}_2}} \right\} \\ = -D_{\text{CO}_2} \frac{\partial [\text{CO}_2]}{\partial x} - D_{\text{R}_2\text{NCOO}^-} \frac{\partial [\text{R}_2\text{NCOO}^-]}{\partial x} \end{aligned} \quad (18)$$

$$\begin{aligned} k_{\text{g}(\text{H}_2\text{S})} \left\{ [\text{H}_2\text{S}]_{\text{g}}^0 - \frac{[\text{H}_2\text{S}]}{m_{\text{H}_2\text{S}}} \right\} \\ = -D_{\text{H}_2\text{S}} \frac{\partial [\text{H}_2\text{S}]}{\partial x} - D_{\text{HS}^-} \frac{\partial [\text{HS}^-]}{\partial x} \end{aligned} \quad (19)$$

$$\begin{aligned} D_{\text{R}_2\text{NH}} \frac{\partial [\text{R}_2\text{NH}]}{\partial x} + D_{\text{R}_2\text{NH}_2^+} \frac{\partial [\text{R}_2\text{NH}_2^+]}{\partial x} \\ + D_{\text{R}_2\text{NCOO}^-} \frac{\partial [\text{R}_2\text{NCOO}^-]}{\partial x} = 0 \end{aligned} \quad (20)$$

$$\frac{\partial [\text{R}_2\text{NCOO}^-]}{\partial x} = 0 \quad (21)$$

$$D_{\text{R}_2\text{NH}} \frac{\partial [\text{R}_2\text{NH}]}{\partial x} + D_{\text{HS}^-} \frac{\partial [\text{HS}^-]}{\partial x} = 0 \quad (22)$$

and

$$K_{\text{H}_2\text{S}} = [\text{HS}^-][\text{R}_2\text{NH}_2^+]/[\text{H}_2\text{S}][\text{R}_2\text{NH}] \quad (2)$$

Equations (18) and (19) balance the transfer rates in gas and liquid phases for CO_2 and H_2S respectively. Equation (20) implies that no amine can cross the interface while eqn. (21) expresses that carbamate (R_2NCOO^-) cannot pass to the gas phase and cannot be converted infinitely fast into CO_2 . Equation (22) gives the analogue of (21) for HS^- , but HS^- may be converted instantaneously into H_2S with simultaneous conversion of R_2NH_2^+ into R_2NH according to reaction (1).

After discretization of the set of partial differential equations (8)–(12) and linearization by a Newton–Raphson technique, the equations are solved iteratively. More details are given in ref. 20.

From Higbie's penetration model equations (8)–(12) a film model description of the mass transfer process is simply obtained by setting the time derivatives on the left-hand sides of (8)–(12) equal to zero. The boundary conditions at the bulk of the liquid phase, at $x = \delta$, are identical to eqns. (13)–(16), (2) and (6), and reflect thermodynamic equilibria in the liquid bulk. The boundary conditions at the interface, at $x = 0$, are identical to eqns. (18)–(22) and (2). The results obtained by the film model thus derived are also included in the evaluation of the experimental results.

Amine depletion and interaction regimes

The mass transfer rates determining reactions (1) and (5) in combination with the mass transfer model are shown schematically in Fig. 1.

In the case of absorption, the species H_2S and CO_2 diffuse from the bulk of the gas phase to the interface. Here, the gas concentrations are in equilibrium with their respective liquid phase concentrations. In the liquid, H_2S and CO_2 diffuse towards the bulk and react simultaneously with the alkanolamine according to eqns. (1) and (5). The ratios of the transfer rates of the species involved, R_2NH and R_2NH_2^+ , to their net conversion rates, determine the extent of depletion of R_2NH and the surplus of R_2NH_2^+ in the penetration zone, and the extent of interaction between the H_2S and CO_2 absorption rates.

The depletion of amine at the interface can be estimated using the approach of Ramachandran and Sharma [7] who used the film theory. The overall accumulation of reaction components similar to those of Ramachandran and Sharma can be obtained by combining the total carbon dioxide (9), sulphur (10), amine (11) and acid (12) accumulations after setting the time derivatives in the left-hand sides of the equations equal to zero:

$$\begin{aligned} D_{\text{R}_2\text{NH}} \frac{d^2 [\text{R}_2\text{NH}]}{dx^2} - D_{\text{H}_2\text{S}} \frac{d^2 [\text{H}_2\text{S}]}{dx^2} \\ - 2D_{\text{CO}_2} \frac{d^2 [\text{CO}_2]}{dx^2} = 0 \end{aligned} \quad (23)$$

Using the following boundary conditions:

$$\text{at } x = 0: [\text{R}_2\text{NH}] = [\text{R}_2\text{NH}]^i \quad \text{and} \quad (24a)$$

Fig. 1. Schema of the process of mass transfer with reactions.

$$[\text{CO}_2] = [\text{CO}_2]^i, \quad [\text{H}_2\text{S}] = [\text{H}_2\text{S}]^i \quad (24b)$$

$$\begin{aligned} J_{\text{H}_2\text{S}} &= -D_{\text{H}_2\text{S}} \frac{d[\text{H}_2\text{S}]}{dx} - D_{\text{HS}^-} \frac{d[\text{HS}^-]}{dx} \\ &= -D_{\text{H}_2\text{S}} \frac{d[\text{H}_2\text{S}]}{dx} + D_{\text{R}_2\text{NH}} \frac{d[\text{R}_2\text{NH}]}{dx} \end{aligned} \quad (25)$$

$$J_{\text{CO}_2} = -D_{\text{CO}_2} \frac{d[\text{CO}_2]}{dx} \quad (26)$$

and at

$$\begin{aligned} x = \delta: \quad [\text{R}_2\text{NH}] &= [\text{R}_2\text{NH}]^0 \quad \text{and} \\ [\text{CO}_2] &= [\text{CO}_2]^0, \quad [\text{H}_2\text{S}] = [\text{H}_2\text{S}]^0 \end{aligned} \quad (27)$$

equation (23) is integrated twice, and we can express the interfacial amine concentration by:

$$\begin{aligned} [\text{R}_2\text{NH}]^i &= [\text{R}_2\text{NH}]^0 + \frac{D_{\text{H}_2\text{S}}}{D_{\text{R}_2\text{NH}}} \{[\text{H}_2\text{S}]^i - [\text{H}_2\text{S}]^0\} \\ &+ 2 \frac{D_{\text{CO}_2}}{D_{\text{R}_2\text{NH}}} \{[\text{CO}_2]^i - [\text{CO}_2]^0\} \\ &- \frac{J_{\text{H}_2\text{S}}}{k_{\text{g}(\text{H}_2\text{S})}} \frac{D_{\text{H}_2\text{S}}}{D_{\text{R}_2\text{NH}}} - 2 \frac{J_{\text{CO}_2}}{k_{\text{g}(\text{CO}_2)}} \frac{D_{\text{CO}_2}}{D_{\text{R}_2\text{NH}}} \end{aligned} \quad (28)$$

By means of eqn. (28) we are able to make a conservative estimate of the maximum amine depletion in the liquid film on the basis of measured H_2S and CO_2 fluxes.

In general, the H_2S molar flux can be expressed as the product of the overall H_2S driving force and the overall mass transfer coefficient k_{ov} , which in turn depends on the gas-side and liquid-side mass transfer coefficients. The H_2S molar flux hence may be described by:

$$\begin{aligned} J_{\text{H}_2\text{S}} &= \frac{[\text{H}_2\text{S}]_{\text{g}}^0 - [\text{H}_2\text{S}]_{\text{l}}^0/m_{\text{H}_2\text{S}}}{[k_{\text{g}(\text{H}_2\text{S})}]^{-1} + [m_{\text{H}_2\text{S}} k_{\text{g}(\text{H}_2\text{S})} f_{\text{H}_2\text{S}}]^{-1}} \\ &= k_{\text{ov}(\text{H}_2\text{S})} \left\{ [\text{H}_2\text{S}]_{\text{g}}^0 - \frac{[\text{H}_2\text{S}]_{\text{l}}^0}{m_{\text{H}_2\text{S}}} \right\} \end{aligned} \quad (29)$$

where

$$m_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}]_{\text{l}}^i}{[\text{H}_2\text{S}]_{\text{g}}^i} \quad (30)$$

and

$$k_{\text{ov}(\text{H}_2\text{S})} = \frac{1}{[k_{\text{g}(\text{H}_2\text{S})}]^{-1} + [m_{\text{H}_2\text{S}} k_{\text{g}(\text{H}_2\text{S})} f_{\text{H}_2\text{S}}]^{-1}} \quad (31)$$

For the single component CO_2 flux, expressions analogous to eqns. (29)–(31) can be derived:

$$\begin{aligned} J_{\text{CO}_2} &= \frac{[\text{CO}_2]_{\text{g}}^0 - [\text{CO}_2]_{\text{l}}^0/m_{\text{CO}_2}}{[k_{\text{g}(\text{CO}_2})]^{-1} + [m_{\text{CO}_2} k_{\text{g}(\text{CO}_2)} f_{\text{CO}_2}]^{-1}} \\ &= k_{\text{ov}(\text{CO}_2)} \left\{ [\text{CO}_2]_{\text{g}}^0 - \frac{[\text{CO}_2]_{\text{l}}^0}{m_{\text{CO}_2}} \right\} \end{aligned} \quad (32)$$

where

$$m_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{l}}^i}{[\text{CO}_2]_{\text{g}}^i} \quad (33)$$

and

$$k_{\text{ov}(\text{CO}_2)} = \frac{1}{[k_{\text{g}(\text{CO}_2})]^{-1} + [m_{\text{CO}_2} k_{\text{g}(\text{CO}_2)} f_{\text{CO}_2}]^{-1}} \quad (34)$$

The enhancement factors $f_{\text{H}_2\text{S}}$ and f_{CO_2} in eqns. (29), (31), (32) and (34) account for the effect of reactions (1) and (5) on the rates of mass transfer of H_2S and CO_2 respectively.

If under simultaneous absorption conditions of H_2S and CO_2 the amine depletion in the (stagnant) film between interface and liquid bulk ($0 \leq x \leq \delta$) or in the penetration zone is negligible, and therefore amine can be supplied at a sufficiently high rate compared to the rates of reactions (1) and (5), the fluxes $J_{\text{H}_2\text{S}}$ and J_{CO_2} are virtually independent of each other. The enhancement factors $f_{\text{H}_2\text{S}}$ and f_{CO_2} may then be calculated from relatively simple analytical solutions of single gas component mass transfer expressions, as summarized in the introduction.

At significant amine depletion, reactions (1) and (5) become interactive through the components R_2NH and R_2NH_2^+ . In this situation H_2S and CO_2 enhancement factors and molar fluxes can only be calculated accurately by mass transfer models like our model [20] which account for this interaction.

A substantial amine conversion by CO_2 and H_2S in combination with a relatively high absorption flux of one of the gas components, e.g. H_2S , gives rise to an interesting feature induced by the interaction of the liquid phase reactions. Owing to the high rate of amine conversion in the penetration zone and the consequent

Fig. 2. Calculated concentration profiles in the penetration zone at $t = \tau$ in a forced desorption example. CO_2 diffuses partly towards the gas phase although, based on the overall driving force, absorption would have been expected.

depletion of amine, the competitive CO_2 -amine reaction is reversed and locally produces amine and free CO_2 . Depending on the transport rate of CO_2 compared with its production rate, the local concentration of CO_2 in the penetration zone can exceed its interfacial concentration and leads to diffusion of part of the CO_2 towards the gas phase (see Fig. 2). The net result will be desorption, although based on the overall CO_2 driving force, absorption would have been expected.

The enhancement factor for CO_2 , calculated from the negative flux and the positive driving force, is consequently negative. Previously we defined this phenomenon as forced desorption [20]. A more extensive elaboration is given in ref. 25.

Selectivity

In gas treatment processes, in many situations it is economically attractive to remove only H_2S from the gas stream, rejecting CO_2 to the highest possible extent, as has been pointed out by, for example, McEwan and Marmin [1]. This overall process selectivity for H_2S , σ_{ov} , is related to the actual local selectivity, σ_{local} , on trays or packing elements by

$$\sigma_{\text{ov}} = \frac{1}{V} \int_0^V \sigma_{\text{local}} dV \quad (35)$$

where σ_{local} is defined by

$$\sigma_{\text{local}} = \frac{\text{rate of absorption of } \text{H}_2\text{S}}{\text{rate of absorption of } \text{CO}_2} = \frac{J_{\text{H}_2\text{S}}}{J_{\text{CO}_2}} \quad (36)$$

As the values of the local selectivity, defined by eqn. (36), depend strongly on the magnitudes of the driving forces of H_2S and CO_2 , generally the selectivity factor S is used as a yardstick for the selectivity:

$$S = \frac{\text{rate of absorption of } \text{H}_2\text{S}}{\text{driving force of } \text{H}_2\text{S}} \times \frac{\text{driving force of } \text{CO}_2}{\text{rate of absorption of } \text{CO}_2} \quad (36)$$

$$= \frac{J_{\text{H}_2\text{S}}}{\{[\text{H}_2\text{S}]_g^0 - [\text{H}_2\text{S}]_l^0/m_{\text{H}_2\text{S}}\}} \times \frac{\{[\text{CO}_2]_g^0 - [\text{CO}_2]_l^0/m_{\text{CO}_2}\}}{J_{\text{CO}_2}} \quad (37)$$

Substitution of the expression for the molar flux $J_{\text{H}_2\text{S}}$ (29) and its analogue for CO_2 (32) into eqn. (37) yields

$$S = \frac{[k_g(\text{CO}_2)]^{-1} + [m_{\text{CO}_2}k_{\ell}(\text{CO}_2)f_{\text{CO}_2}]^{-1}}{[k_g(\text{H}_2\text{S})]^{-1} + [m_{\text{H}_2\text{S}}k_{\ell}(\text{H}_2\text{S})f_{\text{H}_2\text{S}}]^{-1}} = \frac{k_{\text{ov}}(\text{H}_2\text{S})}{k_{\text{ov}}(\text{CO}_2)} \quad (38)$$

which represents, in fact, the ratio of the overall mass transfer coefficients of H_2S and CO_2 .

From eqns. (35)–(38) it is clear that the overall selectivity of an amine treatment process is determined by a number of parameters, namely: mass transfer ($k_{\ell(i)}$, $k_g(i)$), reaction rates ($f_{\text{H}_2\text{S}}$, f_{CO_2}), the solubilities ($m_{\text{H}_2\text{S}}$, m_{CO_2}) and the solvents' equilibrium characteristics ($[\text{H}_2\text{S}]_l^0$, $[\text{CO}_2]_l^0$, or rather the independent parameters $K_{\text{H}_2\text{S}}$ and K_{CO_2}).

For the experiments in the first regime—negligible interaction between H_2S and CO_2 absorption rates—the H_2S mass transfer was entirely gas phase controlled, as was verified using eqn. (31) and the analytical solution of the enhancement factor by Secor and Beutler [9].

The CO_2 absorption appeared to be both gas phase and liquid phase limited. For the CO_2 liquid phase reaction the condition

$$3 < \text{Ha} \ll E_1 \quad (39)$$

where

$$\text{Ha} = \frac{\sqrt{k_2[\text{DIPA}]_l^0 D_{\text{CO}_2}}}{k_{\ell}(\text{CO}_2)} \quad (40)$$

and

$$E_1 = 1 + \frac{D_{\text{DIPA}}[\text{DIPA}]_l^0}{2D_{\text{CO}_2}[\text{CO}_2]_l^0} \quad (41)$$

was fulfilled, and hence [3]

$$f_{\text{CO}_2} = \text{Ha} \quad (42)$$

The selectivity factor for these experiments was simplified, using eqns. (40), (42) and (38), to

$$S = \frac{k_g(\text{H}_2\text{S})}{k_g(\text{CO}_2)} + \frac{k_g(\text{H}_2\text{S})}{m_{\text{CO}_2}\sqrt{k_2[\text{DIPA}]_l^0 D_{\text{CO}_2}}} \approx 1 + \frac{k_g(\text{H}_2\text{S})}{m_{\text{CO}_2}\sqrt{k_2[\text{DIPA}]_l^0 D_{\text{CO}_2}}} \quad (43)$$

Plotting the measured values of S as a function of $k_g(\text{H}_2\text{S})$ should show a linear dependency with slope

$$1/m_{\text{CO}_2} \sqrt{k_2 [\text{DIPA}]_0 D_{\text{CO}_2}}$$

and y axis intercept of unity.

Experimental

Negligible and intermediate interaction regime

The experiments were carried out using an aqueous ~ 2.0 M di-isopropanolamine (DIPA) solution at 25.0°C . In the negligible interaction regime both a stirred cell reactor and a wetted wall column were used. In the intermediate interaction regime only the stirred cell reactor was used.

A sketch of the stirred cell reactor is given in Fig. 3. The reactor consists of two concentric glass cylinders which are sealed on stainless steel 316 top and bottom plates. Water, thermostatted at 25.0°C in an external bath, is pumped around between the double glass wall and in the double wall bottom plate in order to keep the reactor contents at 25.0°C . The gas inlet is tangential and parallel to the gas-liquid interface to prevent uncontrolled disturbance of the surface by inflowing gas. The stirrer is driven by a constant speed motor with variable gear. A set of four baffles prevents the liquid from swirling. By means of an overflow, the liquid level in the reactor is maintained exactly half-way up the second set of stirrer blades. The gas-liquid interface is $68 \times 10^{-4} \text{ m}^2$.

The wetted wall column (see Fig. 4) consists of a precision bore glass tube (inner diameter 0.0100 m) with concentrically fitted stainless steel 316 gas inlet and outlet tubes. The double wall is purged with thermostatted water and controls the temperature of the liquid film. The length of the film can range from 0 to 0.10 m by adjusting the gas outlet tube. Also by means of an

Fig. 4. The wetted wall column.

overflow the liquid level in the reactor was maintained exactly at the edge of the gas outlet tube.

The liquid was fed from an overhead vessel to provide a constant flowrate and was thermostatted before entering the reactors. The flowrates were measured at the reactor outlets by using a calibrated vessel. The N_2 - H_2S and/or CO_2 gas mixtures were thermostatted and saturated at 25.0°C with water before being introduced into the reactors. Gas flows to and from the reactors were measured by means of soap film meters.

The total amine concentration in the solution to the reactors was determined by standard potentiometric titration with 0.500 M HCl . The CO_2 absorption flux in the wetted wall column was obtained via analysis [26-28] of the combined CO_2 , carbamate (R_2NCOO^-) and (bi)carbonate concentrations in the entering and leaving liquid flows. The CO_2 flux in the stirred cell reactor and the H_2S fluxes were obtained via gas chromatographic analyses of the gas flows ($\text{H}_2\text{S} > 1\%$, $\text{CO}_2 > 1\%$ on Porapak-R, $1/8 \text{ in.} \times 2 \text{ m}$, $60 \text{ ml min}^{-1} \text{ He}$, $40-90^\circ\text{C}$, TCD detector; $\text{H}_2\text{S} < 0.5\%$, empty column, $1/8 \text{ in.} \times 2 \text{ m}$, $15 \text{ ml min}^{-1} \text{ He}$, $40-90^\circ\text{C}$, flame photometric detector).

The gas phase mass transfer coefficient k_g in the stirred cell reactor was measured as a function of the stirrer speed by means of absorption of H_2S at low gas phase concentrations into $\sim 2.0 \text{ M DIPA}$ solution (Fig. 5). The k_g for this reactor was obtained by measuring the physical absorption of N_2O into 2.0 M DIPA with a soap film meter and applying the ' $\text{N}_2\text{O}-\text{CO}_2$ analogy' proposed by Laddha *et al.* [29] and Laddha and Danckwerts [23] (Fig. 6).

In the wetted wall column, k_g was determined from the H_2S flux in the simultaneous absorption experiments in the negligible interaction regime. The k_g satisfied the penetration theory. More detailed information on the wetted wall reactor is given in ref. 26.

Fig. 3. The stirred cell reactor.

Fig. 5. The measured k_g in the stirred cell reactor as a function of the stirrer speed.

Fig. 6. The measured k_l in the stirred cell reactor as a function of the stirrer speed.

Extreme interaction regime

The experimental set-up is given in Fig. 7. The stirred cell reactor (only slightly different from the one used in the other experiments) was operated batchwise with respect to the liquid and semi-batchwise with respect to the gas phase.

In the system, the gas phase was circulated by a peristaltic pump over a flow-through cell in an infra-red spectrophotometer for CO_2 detection. Although spectrophotometers are not exceptionally well-suited for quantitative measurements over a wide dynamic range of response, we preferred this type of analysis to, for example, gas chromatography, because it does not influence the gas phase.

Before the experiments, the equipment was purged with nitrogen in order to remove (traces of) oxygen. The experiments started with the introduction of ~ 2.0 M DIPA solution containing ~ 0.30 – 0.35 mol CO_2 /mol DIPA. The amount of CO_2 charged into the solution was determined by the detection limits and sensitivity of

Fig. 7. Set-up for extreme interaction regime experiments.

Fig. 8. A typical example of measured concentration curves during extreme interaction experiments. The H_2S concentration increases because the supply rate is larger than the absorption rate. The CO_2 concentration initially increases owing to forced desorption but CO_2 is reabsorbed after interruption of the H_2S supply.

the infra-red spectrophotometer and the estimated CO_2 gas phase concentration increase. After introduction, the solution was equilibrated at 25°C . Equilibration was checked by means of the spectrophotometer and took some 2 hours.

After this, pure H_2S was introduced into the gas phase at a constant flowrate. The changing gas phase concentrations of H_2S plus CO_2 were recorded by a manometer, whilst the CO_2 concentration alone was determined by the spectrophotometer. Directly on admittance of H_2S , the CO_2 desorbed from the solution into the gas phase. This was unambiguously recorded by the spectrophotometer. The CO_2 desorption increased the CO_2 gas phase concentration immediately to well above its liquid phase equilibrium concentration. In this way a driving force for CO_2 absorption was realized but CO_2 forced desorption was observed.

After ~ 10 – 30 minutes, the H_2S flow was stopped to enable re-equilibration. It was then observed that CO_2 was again absorbed into the solution, virtually to the initial equilibrium (see Fig. 8 for a typical example).

These observations prove unambiguously that the recorded concentration curves in the gas phase are due to reaction processes in the penetration zone alone and have nothing to do with a shift of the bulk equilibrium, which would not have resulted in a re-absorption of CO_2 . The total amount of H_2S introduced into the system was always less than 0.02 mol/mol DIPA and is negligible compared with the CO_2 loading; neither did it shift the original liquid phase equilibrium. Temperature effects in the penetration zone due to heat of reaction were calculated and found to be negligible.

Results

Negligible interaction

In this regime 27 experiments were carried out in a stirred cell reactor and a wetted wall column. The experimental results are summarized in Tables 1(a) and 1(b).

Selectivity factors were calculated from measured molar fluxes of H_2S and CO_2 and the respective—for

TABLE 1(a). Experimental results obtained in the negligible interaction regime with the stirred cell reactor

ϕ_g $\times 10^6$ ($\text{m}^3 \text{s}^{-1}$)	ϕ_l $\times 10^6$ ($\text{m}^3 \text{s}^{-1}$)	Rotor speed (rev min^{-1})	$[\text{CO}_2]_g^{\text{in}}$ (mol m^{-3})	$[\text{CO}_2]_g^{\text{out}}$ (mol m^{-3})	$[\text{H}_2\text{S}]_g^{\text{in}}$ $\times 10^2$ (mol m^{-3})	$[\text{H}_2\text{S}]_g^{\text{out}}$ $\times 10^2$ (mol m^{-3})	k_g $\times 10^3$ (m s^{-1})	S
12.27	1.31	30	1.80	1.43	9.95	4.25	2.4	5.2
12.27	1.31	40	1.80	1.41	9.95	3.69	3.1	6.1
12.27	1.31	50	1.80	1.39	9.95	3.21	3.8	7.1
12.27	1.31	60	1.80	1.37	9.95	2.88	4.4	7.8
11.73	1.33	30	1.88	1.42	8.79	3.88	2.2	3.9
11.73	1.33	40	1.88	1.40	8.79	3.37	2.8	4.7
11.73	1.33	50	1.88	1.39	8.79	2.89	3.5	5.8
11.73	1.33	60	1.88	1.37	8.79	2.50	4.3	6.7
10.43	1.27	30	1.16	0.86	8.06	3.19	2.3	4.4
10.43	1.27	40	1.16	0.84	8.06	2.71	3.0	5.2
10.43	1.27	50	1.16	0.83	8.06	2.32	3.8	6.2
10.43	1.27	60	1.16	0.82	8.06	2.06	4.5	7.0

TABLE 1(b). Experimental results obtained in the negligible interaction regime with the wetted wall column

ϕ_g $\times 10^6$ ($\text{m}^3 \text{s}^{-1}$)	ϕ_l $\times 10^6$ ($\text{m}^3 \text{s}^{-1}$)	L_{ww} $\times 10^2$ (m)	$[\text{CO}_2]_g^{\text{in}}$ (mol m^{-3})	$\Delta[\text{CO}_2]_g$ (mol m^{-3})	$[\text{H}_2\text{S}]_g^{\text{in}}$ $\times 10^2$ (mol m^{-3})	$[\text{H}_2\text{S}]_g^{\text{out}}$ $\times 10^2$ (mol m^{-3})	$k_g(\text{H}_2\text{S})$ $\times 10^3$ (m s^{-1})	S
13.1	0.576	8.0	2.12	4.85	2.66	0.503	9.13	16.6
13.1	0.573	7.0	2.13	4.29	2.66	0.609	9.25	16.7
12.8	0.568	6.0	2.15	3.82	2.67	0.740	9.36	16.3
13.0	0.573	5.0	2.17	3.19	2.67	1.00	8.60	15.2
13.1	0.567	4.0	2.18	2.81	2.67	1.10	9.72	15.9
13.1	0.562	3.0	2.19	2.15	2.69	1.44	9.13	14.8
10.7	2.24	5.0	2.42	0.94	2.77	0.286	16.8	28
10.7	2.19	4.0	2.47	0.69	2.80	0.474	16.4	31
10.7	1.20	5.0	2.45	1.93	2.83	0.507	12.5	19.5
10.7	1.20	4.0	2.46	1.51	2.88	0.724	12.6	20.1
-13.4	0.664	8.0	2.50	4.69	2.68	0.843	6.51	12.4
-13.4	0.667	5.0	2.55	3.08	2.70	1.28	6.73	12.4
-13.4	0.667	3.0	2.61	1.95	2.71	1.69	7.12	12.7
-13.4	1.16	5.0	2.60	1.82	2.71	1.35	6.36	11.5
-13.4	1.16	3.0	2.62	1.24	2.73	1.73	6.89	11.1

Fig. 9. Selectivity factor S as a function of $k_g(\text{H}_2\text{S})$ for the stirred cell reactor and wetted wall column in the negligible interaction experiments.

the wetted wall column experiments logarithmically—averaged gas phase concentrations by using eqn. (37). The selectivity factors thus obtained are plotted in Fig. 9 and show a linear dependency on k_g as predicted by eqn. (43). From the gradient of the fitted line the pseudo-first-order reaction rate constant $k_2[\text{R}_2\text{NH}]$ can be calculated (see eqn. (43)). Using $m_{\text{CO}_2}\sqrt{D_{\text{CO}_2}} = 1.73 \times 10^{-5}$ (2.0 M DIPA [24]), we obtain $k_2[\text{R}_2\text{NH}] = \sim 1.2 \times 10^3 \text{ s}^{-1}$ which is higher than values found in our separate kinetics study [24] ($k_2[\text{R}_2\text{NH}] = \sim 0.8 \times 10^3 \text{ s}^{-1}$). This implies that the measured selectivity factors are lower than would have been predicted on the basis of this kinetics study.

Intermediate interaction

Four series of experiments in the intermediate interaction regime were carried out: constant gas flows con-

TABLE 2. Experimental and calculated data obtained in the intermediate interaction regime

Rotor speed (rev min ⁻¹)	ϕ_g^{in} $\times 10^6$ (m ³ s ⁻¹)	ϕ_g^{out} $\times 10^6$ (m ³ s ⁻¹)	ϕ_c $\times 10^6$ (m ³ s ⁻¹)	$[\text{H}_2\text{S}]_g^{\text{in}}$ (mol m ⁻³)	$[\text{H}_2\text{S}]_g^{\text{out}}$ (mol m ⁻³)	$[\text{CO}_2]_g^{\text{in}}$ (mol m ⁻³)	$[\text{CO}_2]_g^{\text{out}}$ (mol m ⁻³)	$J_{\text{H}_2\text{S}}$ $\times 10^3$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^3$ (mol m ⁻² s ⁻¹)	Film theory calculations		Penetration theory calculations	
										$J_{\text{H}_2\text{S}}$ $\times 10^3$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^3$ (mol m ⁻² s ⁻¹)	$J_{\text{H}_2\text{S}}$ $\times 10^3$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^3$ (mol m ⁻² s ⁻¹)
40	10.00	8.57	1.24	19.82	16.30	0	0	8.60	0	6.65	0	13.24	0
40	9.99	8.70	1.87	19.82	17.78	7.94	8.22	6.37	1.15	4.86	0.98	9.58	2.01
40	9.99	8.65	1.81	19.82	17.94	11.89	12.76	6.30	1.24	4.26	1.32	8.39	2.69
40	9.99	8.75	1.82	19.82	18.69	15.85	16.93	5.07	1.50	3.91	1.54	7.70	3.12
40	10.01	8.76	1.80	19.82	19.23	19.82	20.91	4.40	2.24	3.64	1.72	7.17	3.47
40	10.00	9.53	2.01	0	0	19.82	18.97	0	2.56	0	3.31	0	6.65
40	10.01	9.32	1.78	7.94	7.16	19.82	19.81	1.87	2.02	1.99	2.41	3.87	4.86
40	9.99	9.28	1.80	11.89	11.13	19.82	19.99	2.28	1.84	2.68	2.11	5.26	4.25
40	10.01	9.06	1.71	15.85	15.08	19.82	20.43	3.24	1.96	3.20	1.89	6.29	3.81
40	10.00	8.91	1.83	19.82	18.78	19.82	20.82	4.54	1.87	3.60	1.73	7.09	3.49
60	10.00	8.06	1.87	19.82	14.79	0	0	11.6	0	9.44	0	18.8	0
60	9.99	8.24	1.88	19.82	16.73	7.94	8.41	8.85	1.47	6.73	1.49	13.3	3.03
60	9.99	8.30	1.98	19.82	17.38	11.89	12.98	7.90	1.62	5.95	1.94	11.7	3.94
60	9.99	8.29	1.76	19.82	18.04	15.85	17.33	7.13	2.16	5.42	2.27	10.7	4.58
60	10.01	8.26	1.82	19.82	18.64	19.82	21.48	6.53	3.08	5.04	2.52	9.92	5.08
60	10.00	9.32	2.13	0	0	19.82	18.58	0	3.68	0	4.74	0	9.47
60	10.01	8.94	1.74	7.94	6.65	19.82	19.86	2.95	3.07	2.68	3.51	5.22	7.07
60	9.99	8.90	1.87	11.89	9.84	19.82	20.60	4.59	2.16	3.47	3.17	6.78	6.39
60	10.01	8.59	1.75	15.85	14.28	19.82	20.96	5.29	2.70	4.37	2.78	8.59	5.62
60	10.00	8.48	1.83	19.82	18.12	19.82	21.48	6.55	2.36	4.96	2.55	9.77	5.15

taining 50% H₂S or CO₂ with varying concentrations (0, 20%, 30%, 40% or 50%) of the other acid gas component were fed into the stirred cell reactor at two different stirrer speeds (40 and 60 rev min⁻¹).

In our experimental set-up the entrance gas phase compositions were kept constant. This implies that the prevailing concentration of, for example, H₂S in the reactor increased with rising CO₂ entrance concentration owing to a decrease of the H₂S absorption rate. Consequently, the H₂S driving force for absorption increased with rising CO₂ concentration.

Measured and calculated fluxes are shown in the Table 2 and Figs. 10–13 as a function of the varied gas phase concentration. The calculated fluxes were obtained from the numerical solutions of the penetration and film model equations as given in eqns. (8)–(22). In the Figures, experimental and calculated DIPA molar fluxes are also shown, as obtained from the flux balance equation:

$$J_{\text{DIPA}} = J_{\text{H}_2\text{S}} + 2J_{\text{CO}_2} \quad (44)$$

The differences in fluxes calculated by penetration and film theory are due to the difference, by a factor of ~4,

Fig. 10. Measured and calculated H₂S and DIPA molar fluxes as a function of the CO₂ gas phase concentration in the stirred cell reactor at 40 rev min⁻¹.

Fig. 11. Measured and calculated CO₂ (2X) and DIPA molar fluxes as a function of the H₂S gas phase concentration in the stirred cell reactor at 40 rev min⁻¹.

Fig. 12. Measured and calculated H₂S and DIPA molar fluxes as a function of the CO₂ gas phase concentration in the stirred cell reactor at 60 rev min⁻¹.

Fig. 13. Measured and calculated CO₂ (2X) and DIPA molar fluxes as a function of the H₂S gas phase concentration in the stirred cell reactor at 60 rev min⁻¹.

between the DIPA and CO₂ diffusivities ($D_{\text{CO}_2} = \sim 0.77 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{DIPA}} = \sim 0.19 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) which affects penetration and film calculations in a different way.

In the experiments with 50% H₂S entrance gas phase concentrations (Figs. 10 and 12) measured H₂S and DIPA molar fluxes fall between penetration and film theory calculations. In the 50% CO₂ entrance concentration series, however, measured CO₂ molar fluxes agree better with the film theory (see Figs. 11 and 13).

From the experiments with 50% H₂S entrance concentrations, at both stirrer speeds (Figs. 10 and 12), it is obvious that the measured DIPA molar flux J_{DIPA} , obtained by eqn. (44), remains constant with increasing CO₂ concentration. This implies that for the combined H₂S plus CO₂ molar fluxes the maximum enhancement, determined by complete DIPA diffusion limitation, is realized. This may be verified by rewriting eqn. (28) in the form

$$J_{\text{H}_2\text{S}} + 2J_{\text{CO}_2} = k_R(\text{DIPA})([R_2\text{NH}]^0 - [R_2\text{NH}]^1) + k_{R(\text{H}_2\text{S})}([H_2\text{S}]^1 - [H_2\text{S}]^0) + 2k_{R(\text{CO}_2)}([CO_2]^1 - [CO_2]^0) \quad (45)$$

Substitution of $[R_2NH]^1 = [H_2S]^0 = [CO_2]^0 = 0$ yields exactly the analytical solution for the amine molar flux at simultaneous mass transfer with instantaneous irreversible reactions according to the film theory [7]. In this situation, the maximum J_{DIPA} to the reaction plane is given by

$$J_{DIPA}^{\max} = k_{L(DIPA)}[R_2NH]^0 + k_{L(H_2S)}[H_2S]^1 + 2k_{L(CO_2)}[CO]^1 \approx k_{L(DIPA)}[R_2NH^0] \quad (46)$$

Equation (46) predicts $J_{DIPA}^{\max} = 6.4 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ and $J_{DIPA}^{\max} = 9.1 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$, at 40 and 60 rev min⁻¹ respectively. The average measured DIPA molar fluxes ($J_{DIPA} = 8.6 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ at 40 rev min⁻¹ and $J_{DIPA} = 11.7 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ at 60 rev min⁻¹) exceed these calculated film theory fluxes (see Figs. 10 and 12), but their ratio equals the ratio of the liquid phase mass transfer coefficients (see Fig. 6) at these stirrer speeds:

$$\frac{J_{DIPA}^{40 \text{ rev min}^{-1}}}{J_{DIPA}^{60 \text{ rev min}^{-1}}} = \frac{k_L^{40 \text{ rev min}^{-1}}}{k_L^{60 \text{ rev min}^{-1}}} = 0.72 \quad (47)$$

This confirms that for the 50% H₂S entrance gas phase concentration the amine depletion determines the total mass transfer rate of H₂S plus CO₂. At low H₂S con-

Fig. 14. The selectivity factor at 50% H₂S entrance concentration as a function of the CO₂ gas phase concentration in the stirred cell reactor at 40 rev min⁻¹.

Fig. 15. The selectivity factor at 50% CO₂ entrance concentration as a function of the H₂S gas phase concentration in the stirred cell reactor at 40 rev min⁻¹.

Fig. 16. The selectivity factor at 50% H₂S entrance concentration as a function of the CO₂ gas phase concentration in the stirred cell reactor at 60 rev min⁻¹.

Fig. 17. The selectivity factor at 50% CO₂ entrance concentration as a function of the H₂S gas phase concentration in the stirred cell reactor at 60 rev min⁻¹.

centrations in the 50% CO₂ entrance concentrations (see Figs. 11 and 13), the measured DIPA molar fluxes correspond with the film theory calculations, but at higher H₂S concentrations these tend to higher values than predicted by the film model.

For each experimental run measured and calculated selectivity factors, defined by eqn. (37), are shown in the Figs. 14, 15 (40 rev min⁻¹) and 16, 17 (60 rev min⁻¹). The measured values are rather scattered owing to experimental inaccuracies, but fall between penetration and film model calculations. The film model calculation gives the minimum value of the selectivity factor and therefore it seems preferable to use this model from a conservative absorber design point of view. An increase of the mass transfer coefficients by increasing the stirrer speed improves the selectivity factor (Figs. 14–17) due to the increase of the mass transfer coefficients.

Extreme interaction

Four experimental runs were performed at different stirrer speeds in the stirred cell reactor. The experimental conditions and data are summarized in Tables 3 and 4(a)–(d) respectively.

TABLE 3. Conditions during extreme interaction experiments in the stirred cell reactor

Experiment No.	1	2	3	4
Stirrer speed (rev min ⁻¹)	35	48	55	69
$k_R \times 10^5$ (m s ⁻¹)	0.79	0.94	1.00	1.15
$k_g \times 10^3$ (m s ⁻¹)	2.0	2.4	2.6	3.0
$\alpha_{H_2S} \times 10^3$ start	7	0	4.0	9.4
$\alpha_{H_2S} \times 10^3$ end	14.4	4.0	9.4	19.7
α_{CO_2}	0.357	0.304	0.304	0.304
[DIPA] _{total} (mol m ⁻³)	2140	1970	1970	1970
$V_{liquid} \times 10^6$ (m ³)	730	720	720	720
$V_{gas} \times 10^6$ (m ³)	1094	1104	1104	1104
$\phi_{H_2S} \times 10^6$ (mol s ⁻¹)	6.48 ($t < 30$ min)	6.11 ($0 < t < 2$ min) 10.4 ($2 < t < 10$ min)	10.3 ($0 < t < 8$ min) 15.1 ($8 < t < 11$ min)	10.3 ($0 < t < 20$ min) 12.6 ($20 < t < 23$ min)
$A \times 10^4$ (m ²)	70.4	70.4	70.4	70.4

Since the fluxes are more illustrative than concentrations as a function of time, we derived the molar flux curves from concentration curves as shown in Fig. 8 by numerical differentiation and plotted these in the Figs. 18–21 together with the numerical solutions of penetration and film model calculations. The main conclusion which can be drawn from these Figures is that forced desorption of CO₂ can be realized under practical conditions, and can be predicted by the models. For H₂S the measured fluxes fall, but for a few exceptions, between the calculated ones, while the measured CO₂ forced desorption flux is larger than predicted by the models. In the absorption regime ($J_{CO_2} > 0$) the CO₂ molar flux agrees well with the calculations. This most likely

indicates that the forward reaction rate expression for the CO₂–amine reaction is correct but that the reverse reaction rate—and hence overall rate expression (7)—underestimates the desorption flux. Moreover, it should be kept in mind that the forced desorption part of the calculations is very sensitive to parameters like mass transfer coefficients, diffusion and equilibrium constants, which were obtained from separate experiments and open literature. The experimental errors are amplified by the numerical differentiation of the concentration–time curves.

Fig. 18. Measured and calculated H₂S and CO₂ molar fluxes during extreme interaction experiment 1.

Fig. 19. Measured and calculated H₂S and CO₂ molar fluxes during extreme interaction experiment 2.

TABLE 4(a). Experimental and calculated data obtained in the extreme interaction regime: experiment 1

t (min)	$[H_2S]_g$ (mol m ⁻³)	$[CO_2]_g$ (mol m ⁻³)	J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)	α_{H_2S} $\times 10^3$	α_{CO_2}	Film theory		Penetration theory	
							J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)	J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)
0	0	0.291			7.0	0.357	0	0	0	0
1	0.291	0.305	2.47	-4.92	7.0					
2	0.520	0.329	4.53	-8.29	7.1		3.0	-3.6	5.0	-3.2
3	0.652	0.369	6.42	-9.32	7.3					
4	0.735	0.401	6.30	-8.29	7.5					
5	0.876	0.433	6.72	-7.90	7.6		4.3	-4.3	7.4	-3.5
6	0.927	0.462	7.70	-7.12	7.8					
7	0.992	0.488	7.83	-6.99	8.1					
8	1.033	0.516	8.01	-7.64	8.3					
9	1.084	0.547	7.88	-7.12	8.5					
10	1.135	0.571	8.13	-6.22	8.7		5.1	-3.9	9.0	-2.7
11	1.167	0.595	8.31	-6.60	8.9					
12	1.204	0.622	8.32	-6.80	9.1					
14	1.267	0.673	8.49	-6.15	9.6					
16	1.315	0.717	8.62	-5.37	10.1		5.6	-2.9	9.8	-1.7
18	1.358	0.756	8.75	-4.86	10.5					
20	1.385	0.792	8.83	-3.86	11.0					
25	1.464	0.851	8.81	-2.43	12.0		5.9	2.0	10.5	0.2
30	1.538	0.886			13.4	0.357				
31	1.239	0.886			13.6					
32	0.988	0.884	6.03	1.55	13.8		4.4	2.2	7.4	5.4
33	0.733	0.874	4.51	2.55	13.9					
36	0.373	0.845	2.70	8.11	14.2					
37	0.298	0.792	1.56	11.4	14.2		1.6	7.0	3.0	10.2
39	0.207	0.722	0.932	8.61	14.3					
41	0.154	0.659	0.654	6.93	14.3		0.6	6.1	1.4	8.8
42	0.130	0.637	0.492	6.15	14.4					
44	0.102	0.586	0.259	6.28	14.4					
46	0.090	0.540	0.091	5.89	14.4					
48	0.088	0.495	0.084	5.18	14.4		0.1	3.7	0.6	4.8
50	0.077	0.460	0.077	3.95	14.4					
52	0.076	0.434	0.071	2.91	14.4					
54	0.066	0.415	0.117	2.20	14.4					
56	0.058	0.400	0.110	1.49	14.4		0	1.9	0.2	2.5
58	0.049	0.392	0.062	1.23	14.4					
62	0.048	0.370		1.27	14.4					
65	0.043	0.357		0.95	14.4					
72	0.036	0.336		0.69	14.4					
75	0.037	0.329		0.56	14.4					
80	0.041	0.319		0.39	14.4					
85	0.040	0.314		0.13	14.4					
90	0.029	0.314								

Conclusions

The phenomena during the simultaneous mass transfer of H_2S and CO_2 are classified in three regimes with different extents of interaction.

In the first regime, with negligible interaction, the amine is not depleted in the film or penetration zone. The absorption phenomena can be described by analytical mass transfer expressions in this regime and a simple expression for the selectivity factor is derived for the complete gas phase limitation of H_2S at pseudo-first-order absorption conditions of CO_2 .

In the intermediate interaction regime, the measured H_2S and CO_2 absorption rates and the measured selectivity factors fall between penetration and film model calculations.

In the extreme interaction regime, the existence of forced desorption of CO_2 in practice is demonstrated unambiguously under conditions which can be predicted by the mass transfer models. The H_2S molar fluxes can also be predicted quantitatively, but the forced desorption CO_2 molar fluxes are larger than calculated by the models, possibly due to an incorrect description of the desorption reaction rate.

TABLE 4(b). Experimental and calculated data obtained in the extreme interaction regime: experiment 2

t (min)	$[H_2S]_g$ (mol m ⁻³)	$[CO_2]_g$ (mol m ⁻³)	J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)	α_{H_2S} $\times 10^3$	α_{CO_2}	Film theory		Penetration theory	
							J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)	J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)
0	0	0.143			0	0.304	0	0	0	0
1	0.295	0.145	2.21	-1.44	0.07					
2	0.495	0.154	6.07	-3.40	0.25		4.1	-3.0	6.9	-2.3
3	0.728	0.171	9.01	-5.75	0.52					
4	0.936	0.198	10.1	-7.71	0.82		6.3	-4.6	11.0	-3.3
5	1.09	0.230	11.3	-8.63	1.2					
6	1.20	0.264	11.9	-8.76	1.5		7.5	-4.7	13.0	-3.3
7	1.31	0.297	12.3	-8.63	1.9					
8	1.39	0.330	12.7	-8.23	2.3		8.3	-4.4	14.4	-2.8
9	1.46	0.360	13.1	-7.06	2.6					
10	1.52	0.384	12.9	-6.01	3.0	0.304	8.6	-4.1	15.2	-2.3
10.5	1.28	0.395	12.0	-4.44	3.2					
11	1.06	0.401	9.89	-1.70	3.4		6.6	-1.5	10.6	0.7
12	0.743	0.402	7.16	0.92	3.5					
13.5	0.403	0.390	4.24	2.87	3.8		3.1	3.4	5.1	5.0
14	0.354	0.383	2.36	4.25	3.8					
16	0.189	0.346	1.41	5.29	3.9		1.8	4.2	3.0	5.3
18	0.138	0.302	0.570	5.62	3.9					
19	0.120	0.281	0.314	4.66	3.9					
22	0.102	0.237	0.152	2.81	3.9		0.7	2.0	1.1	2.4
27	0.074	0.203	0.131	1.33	4.0					
32	0.052	0.186	0.086	0.732	4.0					
37	0.041	0.175	0.054	0.405	4.0					
47	0.022	0.166	0.045	0.161	4.0					
56	0.008	0.163

Fig. 20. Measured and calculated H_2S and CO_2 molar fluxes during extreme interaction experiment 3. Fig. 21. Measured and calculated H_2S and CO_2 molar fluxes during extreme interaction experiment 4.

TABLE 4(c). Experimental and calculated data obtained in the extreme interaction regime: experiment 3

<i>t</i> (min)	[H ₂ S] _g (mol m ⁻³)	[CO ₂] _g (mol m ⁻³)	<i>J</i> _{H₂S} × 10 ⁴ (mol m ⁻² s ⁻¹)	<i>J</i> _{CO₂} × 10 ⁵ (mol m ⁻² s ⁻¹)	α _{H₂S} × 10 ³	α _{CO₂}	Film theory		Penetration theory	
							<i>J</i> _{H₂S} × 10 ⁴ (mol m ⁻² s ⁻¹)	<i>J</i> _{CO₂} × 10 ⁵ (mol m ⁻² s ⁻¹)	<i>J</i> _{H₂S} × 10 ⁴ (mol m ⁻² s ⁻¹)	<i>J</i> _{CO₂} × 10 ⁵ (mol m ⁻² s ⁻¹)
0	0	0.164			4.0	0.304	0	0	0	0
1.5	0.609	0.171	6.16	-2.70	4.2					
2	0.730	0.179	9.35	-6.27	4.3		5.5	-4.6	9.6	-3.6
3.5	0.937	0.227	11.1	-9.02	4.8					
4.5	1.08	0.264	11.5	-9.28	5.1					
5	1.15	0.281	12.0	-8.63	5.3		7.6	-5.3	12.7	-4.0
6	1.22	0.313	12.6	-8.10	5.7					
7	1.31	0.343	12.6	-8.63	6.0					
8	1.37	0.379	12.9	-10.5	6.4		8.5	-4.5	15.0	-3.1
9	1.70	0.423	14.6	-12.0	6.8					
10	1.89	0.471	16.0	-11.2	7.3		10.3	-6.3	18.4	-4.7
11	2.11	0.509	15.9	-10.6	7.7	0.304				
12	1.50	0.552	13.1	-5.10	8.2	0.304				
13	1.11	0.548	9.39	3.07	8.5		7.0	5.8	9.3	5.8
15	0.450	0.509	6.17	6.60	9.0					
16	0.308	0.478	3.10	9.28	9.1		3.3	6.8	4.0	7.6
17	0.213	0.438	1.83	9.15	9.2					
20	0.079	0.348	0.736	6.27	9.3		0.5	4.6	1.2	5.6
23	0.044	0.294	0.192	4.18	9.4					
25	0.038	0.266	0.097	2.87	9.4		0	2.8	0.1	3.2
30	0.016	0.226	0.078	1.57	9.4					
35	0.008	0.206		0.732	9.4		0	0.8	0	1.3
45	0	0.190		0.314	9.4					
50	0	0.186		0.235	9.4	0.304				
54	0	0.182								

Nomenclature

<i>A</i>	interfacial area, m ²
<i>D</i>	diffusion coefficient, m ² s ⁻¹
<i>E</i> ₁	infinite enhancement factor defined by eqn. (41)
<i>f</i>	enhancement factor
<i>Ha</i>	Hatta number defined by eqn. (40)
<i>J</i>	molar flux, mol m ⁻² s ⁻¹
<i>k</i> _q , <i>k</i> _g	mass transfer coefficient for liquid and gas phase respectively, m s ⁻¹
<i>k</i> _{ov}	overall mass transfer coefficient (defined by eqns. (29) and (32)), m s ⁻¹
<i>k</i> ₂	forward rate constant of reaction (5), m ³ mol ⁻¹ s ⁻¹
<i>K</i> _{H₂S}	equilibrium constant defined by eqn. (2)
<i>K</i> _{CO₂}	equilibrium constant defined by eqn. (6), m ³ mol ⁻¹
<i>L</i> _{ww}	length of liquid film in wetted wall column, m
<i>m</i>	dimensionless Henry coefficient defined by eqns. (30) and (33)
<i>P</i>	pressure, atm
<i>r</i>	reaction rate, mol m ⁻³ s ⁻¹
<i>S</i>	selectivity factor defined by eqn. (37)
<i>V</i>	volume, m ³
<i>x</i>	distance from interface, m
<i>Z</i>	= 2 <i>x</i> /√π <i>τD</i> _{CO₂} , dimensionless penetration depth
α	loading factor, mol acid gas/mol amine
δ	film thickness according to film theory, m

φ	flowrate, m ³ s ⁻¹
σ _{local}	local selectivity defined by eqn. (36)
σ _{ov}	overall selectivity defined by eqn. (35)
[]	concentration, mol m ⁻³

Indices

ft	film theory
g	gas phase
i	interface
l	liquid
max	maximum
0	bulk
pt	penetration theory

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TABLE 4(d). Experimental and calculated data obtained in the extreme interaction regime: experiment 4

t (min)	$[H_2S]_g$ (mol m ⁻³)	$[CO_2]_g$ (mol m ⁻³)	J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)	α_{H_2S} $\times 10^3$	α_{CO_2}	Film theory		Penetration theory	
							J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)	J_{H_2S} $\times 10^4$ (mol m ⁻² s ⁻¹)	J_{CO_2} $\times 10^5$ (mol m ⁻² s ⁻¹)
0	0	0.182			9.4	0.304	0	0	0	0
1	0.431	0.188	5.20	-2.22	9.5					
2	0.722	0.199	8.49	-4.44	9.7		6.3	-5.2	10.5	-4.1
3	0.901	0.222	11.1	-7.06	10.0					
5	1.09	0.284	12.7	-7.58	10.7		8.4	-5.8	14.4	-4.5
6	1.14	0.311	13.0	-6.53	11.1					
7	1.21	0.334	13.0	-6.01	11.5					
8	1.26	0.357	13.6	-5.75	11.9					
9	1.29	0.378	14.0	-5.36	12.3		9.2	-5.2	15.3	-3.4
10	1.31	0.398	14.2	-5.36	12.7					
11	1.32	0.419	14.2	-5.10	13.1					
12	1.34	0.437	14.1	-4.57	13.5					
13	1.36	0.454	14.4	-3.92	14.0		9.5	-4.2	16.8	-2.0
14	1.36	0.467	14.6	-3.53	14.4					
15	1.36	0.481	14.3	-3.66	14.8					
16	1.39	0.495	13.8	-3.66	15.2					
17	1.42	0.509	14.1	-3.79	15.7					
18	1.43	0.524	14.4	-3.53	16.1		9.6	-3.1	17.2	-0.8
19	1.43	0.536	14.2	-3.40	16.5					
20	1.46	0.550	14.4	-4.84	16.9					
21	1.58	0.573	15.1	-5.36	17.4					
22	1.67	0.591	15.6	-4.05	17.8		10.4	-3.7	18.4	-1.1
23	1.76	0.604	15.1	-2.61	18.3	0.304				
24	1.21	0.611	12.6	0.261	18.7					
25	0.790	0.602	9.20	4.57	19.1		6.0	3.1	10.5	6.7
26	0.502	0.576	5.88	8.62	19.3					
27	0.340	0.536	3.53	10.1	19.4		2.9	6.7	4.8	8.6
28	0.232	0.499	2.17	10.5	19.5					
29	0.174	0.456	1.20	10.7	19.6					
30	0.140	0.417	0.575	10.3	19.6		0.9	5.7	1.6	6.7
31	0.130	0.377	0.523	7.19	19.6					
32	0.100	0.362	0.562	4.31	19.6					
34	0.074	0.326	0.340	4.70	19.6		0.2	3.7	0.4	4.2
35	0.061	0.308	0.204	3.44	19.6					
45	0.035	0.225	0.037	1.48	19.6					
50	0.034	0.210	0.123	6.53	19.6					
55	0	0.200			19.7					

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