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MODELLING OF SIMULTANEOUS MASS AND HEAT TRANSFER WITH CHEMICAL REACTION USING THE MAXWELL-STEFAN THEORY—II. NON-ISOTHERMAL STUDY

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Abstract—In Part I a general applicable model has been developed which calculates mass and heat transfer fluxes through a vapour/gas–liquid interface in case a reversible chemical reaction with associated heat effect takes place in the liquid phase. In this model the Maxwell–Stefan theory has been used to describe the mass transport. Also in Part I the isothermal absorption of a pure gas A in a solvent containing a reactive component B has been studied. In this paper the influence of thermal effects on the mass transfer rates is investigated, with special attention to the concentrated systems. The thermal effects arise as a consequence of enthalpy changes due to phase transitions and chemical reaction. Account is taken of the influence of temperature gradients on (i) the solubility of the gaseous component in the liquid phase, (ii) the chemical reaction rate and (iii) the mass transfer coefficients in the liquid phase. Numerical simulations show that, when compared to the corresponding isothermal case, the thermal effects can affect the mass transfer rates by as much as a factor of 30. In case of high Lewis numbers the numerically calculated mass transfer rates can very well be predicted from an approximate analytical expression, which has been presented in this paper. In most cases this is also a reasonable estimate of the mass transfer rate in case the Lewis number equals unity. In case of a second-order chemical reaction it was shown that thermal effects may change the maximum enhancement factor and consequently shift the absorption from the instantaneous regime to the pseudo-first-order regime. Further, it is concluded that there may exist non-isothermal gas–liquid absorption systems where minor changes in parameters appearing in the heat balance, e.g. binary mass transfer coefficients, chemical reaction rate constant, *Le'* number or heat transfer coefficients, may result in drastically altered system behaviour. For situations in which thermal effects are significant, also the vaporization of the liquid mixture should be taken into account, especially when the calculated interface temperature is near or exceeds the boiling temperature of the liquid.

1. INTRODUCTION

Many industrial processes involve mass transfer processes between a gas or a vapour and a liquid. Often in such processes thermal effects are important. Thermal effects arise from phase changes accompanying absorption, desorption, condensation or evaporation. Chemical reactions, if occurring in the liquid phase, also contribute to enthalpy changes. Reactive distillation is a typical example in which mass and heat transfer processes between the vapour and liquid phases are to be considered simultaneously with liquid-phase chemical reaction.

In Part I (Frank *et al.*, 1995) a general applicable model has been developed which calculates mass and heat transfer rates through a vapour/gas–liquid interface in case a reversible chemical reaction with associated heat effect takes place in the liquid phase. In this model the Maxwell–Stefan theory has been implemented to describe the mass transport. The description of the transfer processes has been based on the film model according to which each phase is thought to exist of a well-mixed bulk and a stagnant zone in the latter of which simultaneous transport of heat and mass occurs. In Part I isothermal simulations have been conducted to show the important features of the model for mass transfer with chemical reaction. When the concentration of the transferring species in the liquid phase is high, the mass transfer of each species will be influenced by the movement of the other transferring species and a proper formulation of the diffusion equations using the Maxwell–Stefan theory becomes important. In this paper the influence of heat effects on these (chemically enchanced) mass transfer processes will be investigated.

Heat is generated when a gas absorbs in the liquid, due to release of heat of dissolution. Heat is also generated when exothermic chemical reactions take place in the liquid phase. Such heat effects will cause a temperature gradient to develop near the gas–liquid interface. The developed temperature profile will influence (i) the solubility of the dissolving component, (ii) the chemical reaction rate constant, and (iii) the diffusivities of the transferring species in the liquid phase. As the mass transfer rate depends on all these

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parameters, this rate will change due to aforementioned heat effects.

In the literature several studies concerning simultaneous mass and heat transfer with chemical reaction have been reported: Shah (1972), Mann and Moyes (1977), Allan and Mann (1979, 1982) Asai *et al.* (1985), White and Johns (1986), Bhattacharya *et al.* (1987, 1988), Chatterjee and Altwicker (1987), Evans and Selim (1990), Al-Ubaidi *et al.* (1990) and Al-Ubaidi and Selim (1992). None of these studies has employed the Maxwell–Stefan formulation of diffusion and therefore their validity is strictly limited to cases of low concentration of transferring species in the liquid phase. The transfer models used in the literature can be divided into three broad categories:

(A) Models based on the penetration theory which is based on non-stationary description of the transfer processes. From these models it follows that in liquids normally the heat penetration depth considerably exceeds the mass penetration depth, i.e. $\alpha \gg D_{ij}$, and consequently it is generally assumed that the mass transfer processes take place at a constant temperature, i.e. the interface temperature. Due to this assumption the heat and mass balances are decoupled and can be solved independently.

(B) Models based on the film theory with the assumption of identical effective film thicknesses for heat and mass, i.e. $\delta_h = \delta_m$. The advantage of this model type is the less involved mathematics in comparison to the penetration-type models, but the fact that the mass transfer zone and the heat transfer zone do not necessarily coincide poses a conceptual difficulty.

(C) Models based on the film theory which define a stagnant zone for the mass transfer processes and one with a much larger thickness for the heat transfer processes, i.e. $\delta_h \gg \delta_m$.

The primary goal of this paper is to study systematically the influence of heat effects on chemically enhanced absorption. The film model is adopted without making assumptions with respect to $Le' = \delta_h/\delta_m$. Both first- and second-order reactions will be considered, without making assumptions of the prevailing reaction regime. In addition the Maxwell–Stefan theory will be used to describe the mass transfer processes. The importance of incorporating thermal effects will be demonstrated by comparing the results of the isothermal model with model calculations in which non-isothermal effects are properly taken into account.

2. THEORY

In Part I a numerical study has been conducted of the isothermal absorption of a pure gas A in a solvent containing a reactive component B. In this paper the same absorption system (see Fig. 1) will be considered in detail under non-isothermal conditions. Component A is allowed to react by a unimolecular exothermal chemical reaction or by a bimolecular exothermal chemical reaction with component B to produce C. The chemical reactions taking place are, respectively,

$$A \rightarrow C \tag{1}$$

and

$$A + B \rightarrow C \tag{2}$$

where the respective reaction kinetics are described by

$$R = k_1 x_A \tag{3}$$

and

$$R = k_1 x_A x_B. \tag{4}$$

It is assumed that the solvent, component B and product C are not volatile and that the fractions of A and C in the liquid bulk equal zero. Due to absorption as well as chemical conversion heat will be produced in the liquid-phase mass transfer film, which will subsequently be transported to the liquid bulk. First some comments will be given about the influence of the heat effects.

As mentioned before there are two possible sources of heat. At first, heat production due to phase change

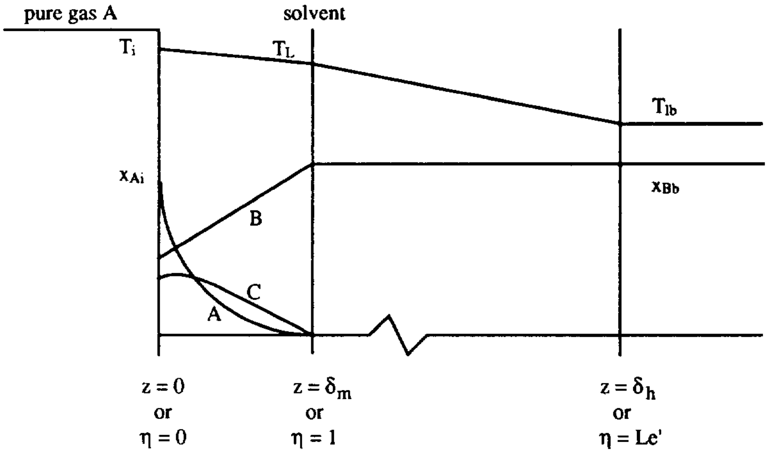

Fig. 1. Schematic representation of the fraction and temperature profiles in the mass and heat transfer film for the gas–liquid absorption system.

has to be considered. This effect is accounted for in the partial molar enthalpies of component A for both phases and defined by

$$H_A = H_{A,T_{\text{ref}}} + C_{p,A}(T - T_{\text{ref.}}). \tag{5}$$

In eq. (5) it is assumed that H_A is a linear function of temperature T, whereas $H_{A,T_{\text{ref}}}$ and $C_{p,A}$ are constants which will differ for the gas and liquid phase. In our simulations it has been assumed that $C_{p,A}$ equals zero for both phases and in this case the heat of solution ΔH_s can be expressed as

$$\Delta H_s = H^{\text{gas}}_{A,T_{\text{ref.}}} - H^{\text{liq}}_{A,T_{\text{ref.}}} \tag{6}$$

which is independent of temperature.

The second source of heat is the one due to chemical reaction. This effect also can be incorporated in the partial molar enthalpies by taking all heat capacities equal to zero and setting $H_{i,T_{\text{ref.}}}$ of the liquid phase to their appropriate values. As a consequence the heat of reaction ΔH_R is given by

$$\Delta H_R = -\sum_{i=A,B,C} v_i H_{i,T_{\text{ref.}}} \tag{7}$$

which is also independent of temperature.

Heat effects will cause temperature changes and therefore influence the physical and chemical parameters. It is generally assumed that there are three important parameters which are sensitive to temperature changes. These are the solubility of A in the liquid m_A, the chemical reaction rate constant k_1 and the binary mass transfer coefficients K_{ij}. These dependencies have been incorporated in our numerical model by using the following Arrhenius type of equations:

$$m_A = m_{A,0}\exp\left[\frac{E_s}{R_{\text{gas}}}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{8}$$

$$k_1 = k_{01}\exp\left(\frac{-E_{a1}}{R_{\text{gas}}T}\right) \tag{9}$$

$$K_{ij} = K_{ij,0}\exp\left[\frac{-E_D}{R_{\text{gas}}}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]. \tag{10}$$

The temperature dependencies are thus determined by setting the values E_s, E_{a1} and E_D. By using eq. (10) it is assumed that all binary mass transfer coefficients have the same activation energy of diffusion.

Due to the non-linearity of the model equations their exact analytical solution is not possible, which necessitates the use of a numerical solution procedure. However, in addition the development of approximate explicit analytical expressions, which can be used as an alternative to the numerical model, will be carried out in the study. For this purpose it has been assumed that the thickness of the heat transfer film significantly exceeds the thickness of the mass transfer film ($Le' \gg 1$). If Le' becomes very large the mass and heat balance can be decoupled and the heat flux generated in the mass transfer film can be imposed as a boundary flux for the heat transfer film. In that case the mass transfer equations should be solved at the interface temperature which can be performed analytically. This will result in exact implicit analytical expressions for the absorption flux N_A. Due to their ease of use we prefer explicit analytical expressions and therefore the following approximate explicit expressions for the absorption flux of A through the gas–liquid interface N_A (see Part I) have been developed:

—absorption without chemical reaction:

$$N_A = \frac{-K_{As}c_T\ln(1 - x_{Ai})}{1 + x_{Bb}(d_{AB} - 1)} \tag{11}$$

—absorption with instantaneous bimolecular chemical reaction:

$$N_A = \frac{K_{As}c_T x_{Bb}}{(d_{BC} - d_{Bs})x_{Bb} + d_{Bs}} - \frac{K_{As}c_T\ln(1 - x_{Ai})}{(d_{AC} - 1)x_{Bb}\dfrac{d_{Cs} + (d_{BC} - d_{Cs})x_{Bb}}{d_{Bs} + (d_{BC} - d_{Bs})x_{Bb}} + 1} \tag{12}$$

—absorption with chemical reaction:

$$N_A = E_A(N_A)_{\text{eq.(11)}} \tag{13}$$

where the enhancement factor E_A is expressed for a first-order unimolecular chemical reaction as

$$E_A = \frac{Ha}{\tanh(Ha)} \tag{14}$$

where the expression for the Hatta number Ha is given by

$$Ha = \sqrt{\frac{k_1\delta_m}{c_T K_{A\text{eff}}}}. \tag{15}$$

In the expression for the Hatta number the effective mass transfer coefficient of A in the liquid mixture $K_{A\text{eff}}$ is defined for this absorption system as follows:

$$\frac{1}{K_{A\text{eff}}} = \frac{x_{Bb}}{K_{AB}} + \frac{1 - x_{Bb}}{K_{As}}. \tag{16}$$

The enhancement factor E_A for a second-order bimolecular chemical reaction is expressed as

$$E_A = \frac{Ha\sqrt{\dfrac{E_{A\infty} - E_A}{E_{A\infty} - 1}}}{\tanh\left(Ha\sqrt{\dfrac{E_{A\infty} - E_A}{E_{A\infty} - 1}}\right)} \tag{17}$$

where Ha and $E_{A\infty}$ are, respectively, given by

$$Ha = \sqrt{\frac{k_1 x_{Bb}\delta_m}{c_T K_{A\text{eff}}}} \tag{18}$$

and

$$E_{A\infty} = \frac{(N_A)_{\text{eq.(12)}}}{(N_A)_{\text{eq.(11)}}}. \tag{19}$$

It should be kept in mind that all temperature-dependent parameters in eqs (11)–(19) must be evaluated at the interface temperature. This interface temperature follows from the heat balance over the heat transfer film. Heat generated due to absorption and chemical conversion in the mass transfer film have to be conducted through the heat transfer film to the liquid bulk (heat losses to gas bulk are neglected) and leads to the following heat balance:

$$N_{A,0}\Delta H_s + (N_{A,0} - N_{A,\delta})\Delta H_R = h_l(T_i - T_b) \quad (20)$$

where $N_{A,0}$ represents the flux through the gas–liquid interface and is expressed by eq. (13). $N_{A,\delta}$ represents the mass flux of A through the mass transfer film–bulk interface, i.e. the part of $N_{A,0}$ which has not been converted in the mass transfer film. No expression is yet available for $N_{A,\delta}$ in case the Maxwell–Stefan theory is used to describe the mass transfer. Similar to the derivation of the enhancement factor in Part I, the classical theory [see e.g. Westerterp *et al.* (1990)] has been applied as a starting point. In case Fick's law is used to describe mass transfer with first-order unimolecular chemical reaction, $N_{A,\delta}$ is given by

$$N_{A,\delta} = \frac{Ha}{\sinh(Ha)}(N_A)_{\text{without reaction}} \quad (21)$$

where the expression for Ha is given by eq. (15). Now it is assumed, similar to the expression of the enhancement factor, that eq. (21) is also valid in case the Maxwell–Stefan theory is used to describe the mass transfer. The mass flux of A in absence of chemical reaction is given by eq. (11). As for second-order bimolecular chemical reactions such equations do not exist, it is also assumed that eq. (21) holds for second-order reactions, where Ha now is defined by eq. (18). This assumption will become more accurate at higher values of the infinite enhancement factor $E_{A\infty}$.

From eqs (11)–(21) the absorption flux of A through the gas–liquid interface can be calculated, taking into account heat effects and the diffusional interactions between the transferring species. In addition the interface temperature will be given. The equations can be solved iteratively until the absorption flux and the interface temperature satisfy some convergence criterion. Summarizing it should be kept in mind that these results are based on the following assumptions:

—$Le' \gg 1$, i.e. the thickness of the heat transfer film is much larger than the thickness of the mass transfer film.

—The approximate analytical expressions for the absorption flux under isothermal conditions are valid. This has been shown in Part I.

—The approximate expression for the mass flux at the mass transfer film–bulk interface, deduced from classical theory for mass transfer with first-order reaction, is valid for both first- and second-order chemical reaction using the Maxwell–Stefan theory. This has still to be proved.

3. RESULTS

With the numerical model described in Part I simulations were performed for the non-isothermal absorption of a pure gas A in a solvent containing a component B (see Fig. 1). The parameter values used in the simulations are given in Table 1.

The influence of the heat effects, due to absorption and chemical reaction, on the mass transfer rates has been studied in detail by comparing the results of the non-isothermal absorption simulations ($Le' = 10$) with the results of isothermal absorption simulations. This comparison has been carried out systematically by giving one of the parameters E_{a1}, E_s or E_D a value differing from zero and taking the other two parameters of this set equal to zero. By following this approach the effect of each temperature-dependent parameter on the mass transfer rate could be studied independently. In addition simulations were carried out in which all three parameters (i.e. E_{a1}, E_s and E_D) differed from zero.

Two sets of binary mass transfer coefficients have been used to perform the study. In one of the sets, all binary mass transfer coefficients were taken equal and

Table 1. Parameter values used to calculate the data points shown in Figs 2–7 for absorption of a pure gas A into a solvent containing component

$\delta_m = 1 \times 10^{-5}$ m
$H^{\text{gas}}_{0,i\to i,T_{\text{ref.}}} = 50{,}000$ J/mol

$c_T = 1 \times 10^4$ mol/m^3
$H^{\text{liq}}_{0,i\to i,T_{\text{ref.}}} = 0$ J/mol

$C_{p,i} = 0$ J/mol K
$H^{\text{liq}}_{0,i\to i,T_{\text{ref.}}} = 0$ J/mol

$T_{lb} = 300$ K $h_l = 500$ J/K s
$H^{\text{liq}}_{0,i\to i,T_{\text{ref.}}} = -100{,}000$ J/mol

$Le' = 1$ or 10

$E_s = 0$ or 25,000 J/mol

$E_{a1} = 0$ or 25,000 J/mol

$E_D = 0$ or 10,000 J/mol

Reaction scheme 1
A → C

Reaction scheme 2
A + B → C

Equal binary mass transfer coefficients
$K^l_{ij} = 1 \times 10^{-4}$ m/s $i =$ A,B,C,s $j =$ A,B,C,s

Different binary mass transfer coefficients
$K^l_{AB} = 3 \times 10^{-4}$ m/s $K^l_{AC} = 3 \times 10^{-5}$ m/s
$K^l_{As} = 1 \times 10^{-4}$ m/s
$K^l_{BC} = 4 \times 10^{-4}$ m/s $K^l_{Bs} = 5 \times 10^{-5}$ m/s
$K^l_{Cs} = 2 \times 10^{-4}$ m/s

Composition regime 1
$x_{Ai0} = 0.003$ and $x_{Bb} = 0.006$

Composition regime
$x_{Ai0} = 0.003$ and $x_{Bb} = 0.6$

Composition regime 3
$x_{Ai0} = 0.3$ and $x_{Bb} = 0.6$

in this case the effective mass transfer coefficient of A in the solvent mixture was composition independent. The second set has been chosen to provide an extreme test for using the concept of composition weighted reciprocal mass transfer coefficients to yield the effective transfer coefficient K_{Aeff} in the expression for the Hatta number [eq. (15)]. Besides, three composition regimes were considered in the simulations. The first one, with low values of x_{Ai} and x_{Bb}, will reduce the Maxwell–Stefan solution to the solution obtained on basis of Fick's first law. This is also valid for the second composition regime with low x_{Ai} and high x_{Bb}, however in this regime we have to correct for the effective mass transfer coefficient of A. In the second composition regime, the bimolecular reaction can be described as a pseudo-first-order reaction with respect to component A. The third regime with high values of both x_{Ai} and x_{Bb} will lead to interactions between all components present in the liquid phase and as a consequence Fick's law will not be valid anymore which necessitates the use of the Maxwell–Stefan theory as already shown in Part I.

As Le' is given a high value of 10, the approximate analytical solution derived in the previous section for $Le' = \infty$ is expected to be valid with a reasonable degree of accuracy. Whether this is indeed the case will be studied for all simulations described above. In addition the effect of Le'-number on the mass transfer rate will be studied by comparing the numerical results of simulations for $Le' = 10$ with numerical results of simulations for $Le' = 1$. From this comparison it can also be concluded in which cases the approximate analytical solution can be used in case $Le' = 1$. In comparing the results for $Le' = 10$ with the ones for $Le' = 1$, the thickness of the mass transfer film δ_m is kept constant to maintain the same value for the Hatta number. However, the heat transfer coefficient $h_l = \lambda/\delta_h$, which appears in the heat balance [eq. (20)], should also be kept constant to enable proper comparison. Due to the fact that δ_h changes for different Le' values, λ should be adapted to maintain constant h_l values.

Subsequently the results of the simulations will be presented. Numerically and analytically computed results will be represented in graphical form where in each figure calculated values of the dimensional absorption flux of A, defined as the ratio of the absorption flux of A and the absorption flux of A for the corresponding isothermal case without chemical reaction, are shown as a function of the dimensionless Hatta number for the following situations:

1. isothermal absorption,
2. non-isothermal absorption with $Le' = 10$,
3. non-isothermal absorption with $Le' = 1$.
4. absorption system described by approximate analytical expressions (11)–(21)

Comparison of simulations with equal and different binary mass transfer coefficients

From the results which will be presented below it became evident that the influence of heat effects on the absorption flux was not biased by the particular choice of the set of binary mass transfer coefficients. Generally, it could be concluded that the differences between the numerical results for $Le' = 1$ and those for $Le' = 10$ were not affected at all and additionally that the differences between the results obtained from the analytical expression and the numerically computed results for $Le' = 10$ increase to a small extent if different instead of equal binary mass transfer coefficients are used. This is probably due to the approximate nature of eqs (11)–(19) and (21), which becomes more pronounced in case of different binary mass transfer coefficients.

Therefore, only the results of the simulations with different binary mass transfer coefficients will be discussed below in detail. In case striking differences between the two sets (i.e. the equal and different coefficients) have been found, this will be indicated.

Temperature-dependent solubility

In this case E_{a1} and E_D were set equal to zero, whereas E_s was given a value of 25,000 J/mol. The solubility of the pure gas A is given by the value of x_{Ai}. From eq. (8) it follows that higher interface temperatures will result in a lower solubility. As x_{Ai} decreases, the driving force for mass transfer decreases and consequently the absorption flux of A will also decrease at higher interface temperatures. The results of the simulations are presented in Figs 2(a) and (b) which show the dimensionless absorption flux $\mathscr{E}$ of component A as a function of the Hatta number.

It turned out that the results for first-order chemical reaction with low solubility of A and the results for second-order chemical reaction with low solubility of A and an excess of B present in the liquid phase (i.e. pseudo-first-order chemical reaction with respect to A) were very similar. Therefore, only the results of the latter case are shown [see Fig. 2(a), $x_{Bb} = 0.6$]. Low solubilities of A result in low physical absorption fluxes and hence in a low heat production rate. Therefore no significant change in interface temperature occurs and consequently heat effects do not play a role. With increasing chemical reaction rate, i.e. increasing Hatta number, enhancement of mass transfer occurs resulting in an increased heat production rate which causes an increasing deviation between results corresponding to isothermal conditions and the numerical results obtained for $Le' = 10$. Thus, for high reaction rates one has to take into account heat effects. Further it can be concluded that in this case the value of Le' has no effect on the absorption flux. This is due to the fact that at high chemical reaction rates the absorption heat as well as the reaction heat is released at the interface for both $Le' = 10$ and $Le' = 1$. Since in this case x_{Ai} is the only temperature-dependent quantity, not the temperature profile in the mass transfer film but the interface temperature, which is independent of Le', becomes important. In case of a second-order chemical reaction with low solubility of A and low maximum enhancement factor

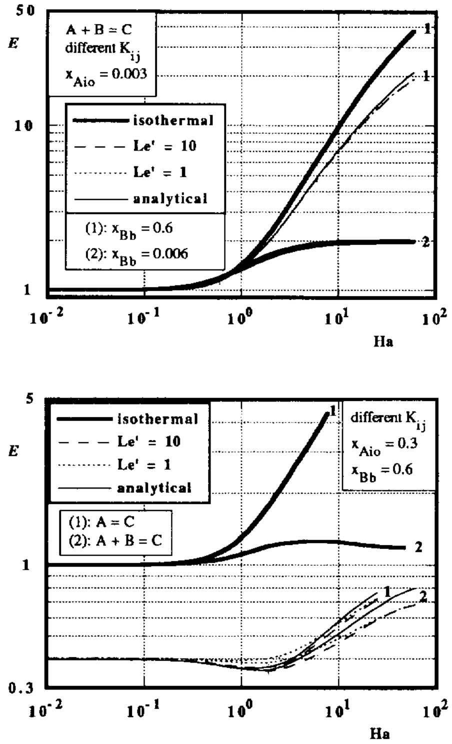

Fig. 2. Dimensionless absorption flux $\mathscr{E}$ of component A obtained from the numerical model and the analytical expressions as a function of the Hatta number in case the solubility is temperature dependent: (a) second-order chemical reaction, different binary mass transfer coefficients and second composition regime; (b) first-order and second-order chemical reaction, different binary mass transfer coefficients and third composition regime. Parameter values are given in Table 1.

($x_{Bb} = 0.006$) heat effects are insignificant for any chemical reaction rate constant since the absorption flux is limited due to the low maximum enhancement factor.

Figure 2(b) shows the results in case A possesses a high solubility. In this case even the physical absorption flux of A is large enough to change the interface temperature and thus the solubility, significantly. If the heat balance is not taken into account an error of 150% with respect to the absorption flux will be made. If a first-order chemical reaction proceeds, this error will increase strongly at high reaction rates. For a second-order chemical reaction it can be seen from Fig. 2(b) that for non-isothermal absorption the mass transfer rate has not reached its maximum attainable value. This is due to the fact that with increasing the Hatta number also the maximum enhancement factor increases due to the lowered solubility of A. As a consequence, the maximum enhancement factor will be attained at higher *Ha* values. For both reaction schemes the influence of *Le'* is most important at intermediate Hatta numbers which is expected behaviour since in this situation the heat of reaction is released in the entire mass transfer film. For $Le' = 10$ this will be felt as a boundary heat production, whereas for $Le' = 1$ this is not the case and accordingly the interface temperature and solubility of A change. The differences are however small (10%). At both low and high *Ha* values heat is released close to the interface and will be experienced as a boundary heat flux.

The analytical expression produces good results in all three composition regimes and for both reaction schemes: the maximum observed deviation being 15% in the third composition regime of the second-order chemical reaction. This error is most probably caused by the approximate nature of the mass transfer equations.

Temperature-dependent binary mass transfer coefficients

In this case E_{a1} and E_s were set equal to zero, whereas E_D was given a value of 10,000 J/mol. From eq. (10) it follows that heat production will result in higher binary mass transfer coefficients and hence will increase the mass transfer rate of component A. The results of the simulations are presented in Figs 3(a)–(c).

Figure 3(a) shows the results for pseudo-first-order chemical reaction with low solubility of A. In absence of chemical reaction heat effects have no influence, which is due to the very low heat production rate. With increasing chemical reaction rate the difference between the results for isothermal and non-isothermal conditions becomes more pronounced and eventually as high as 70%. Moreover, it can be seen that the value of *Le'* has a marked influence on absorption rate. The difference between the results for $Le' = 1$ and $Le' = 10$ increase with increasing *Ha*, but remains always smaller than the difference between the results for $Le' = 10$ and the results for isothermal absorption. In case of $Le' = 10$ the mass transfer coefficient will only be affected by the interface temperature whereas for $Le' = 1$ the entire temperature profile will affect the mass transfer process, resulting in lower mass transfer rates. The analytical expressions produce maximum errors of 30%.

Figures 3(b) and (c) show the results for mass transfer with first-order chemical reaction corresponding to the third composition regime where, respectively, different [Fig. 3(b)] and equal [Fig. 3(c)] binary mass transfer coefficients have been used. Due to high solubility of A large differences between non-isothermal absorption for $Le' = 10$ and isothermal absorption already exist at low *Ha* values. By examining the influence of the *Le'* value it follows that for high values of the Hatta number, the results for $Le' = 1$ and $Le' = 10$ approach each other. This is caused by the shape of the concentration profile of component A. The effective film thickness for component A decreases due to enhancement and consequently the temperature which affects the mass transfer coefficient of A will approach the interface temperature. The analytical expression predicts the absorption rate very well for most *Ha* values, but a maximum error of 50% in case of equal mass transfer coefficients and intermediate *Ha* values is somewhat high. This is probably

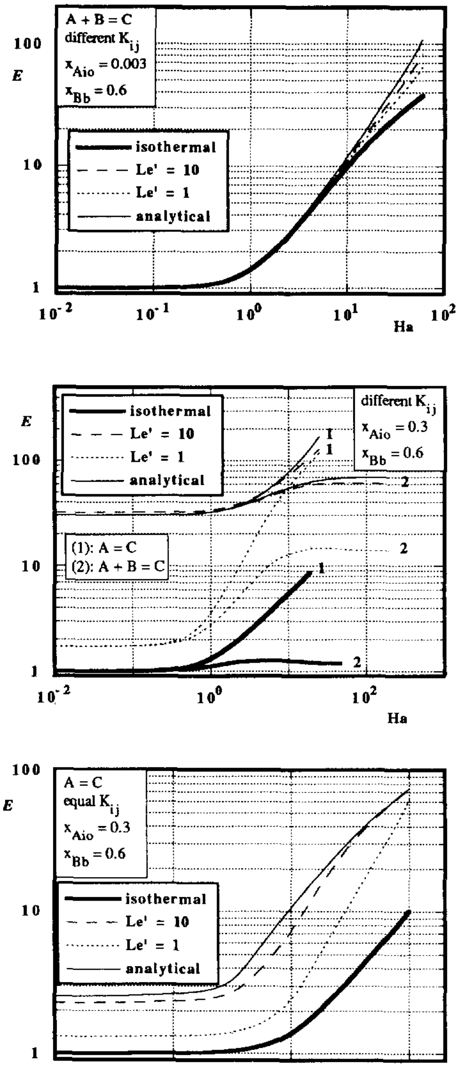

Fig. 3. Dimensionless absorption flux $\mathscr{E}$ of component A obtained from the numerical model and the analytical expressions as a function of the Hatta number in case the binary mass transfer coefficients are temperature dependent: (a) second-order chemical reaction, different binary mass transfer coefficients and second composition regime; (b) first-order and second-order chemical reaction, different binary mass transfer coefficients and third composition regime; (c) first-order chemical reaction, equal binary mass transfer coefficients and third composition regime. Parameter values are given in Table 1.

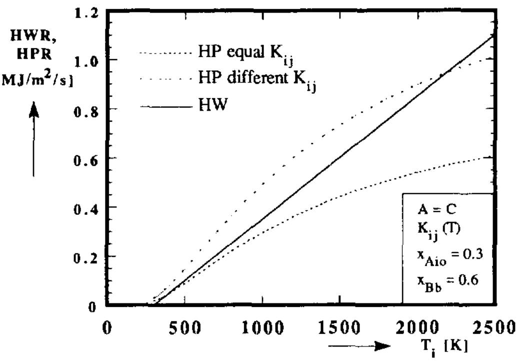

Fig. 4. Heat withdrawal rate (HWR) and heat production rate (HPR) as a function of the interface temperature T_i calculated from the analytical expressions in case of first-order chemical reaction, equal or different binary mass transfer coefficients and third composition regime. Parameter values are given in Table 1.

due to a small error in calculating N_δ from eq. (20) which causes an error in the heat production rate and thereby in the interface temperature. As a consequence the interface flux of A N_0 will also change.

An unexpected very large increase in the computed absorption rate was found when the effective mass transfer coefficient of A was increased by a factor of 1.67 [eq. (16), by taking different instead of equal binary mass transfer coefficients] in case of non-isothermal physical absorption for $Le' = 10$. This striking phenomenon can be explained by examining eq. (20). This equation demands a balance between the heat production rate per unit area and the heat flux entering the liquid bulk. Both quantities depend on the value of the interface temperature T_i which has to satisfy eq. (20). This interface temperature T_i can be determined graphically by plotting the left- and right-hand side of this equation as function of T_i. This has been done for the systems corresponding to Figs 3(b) and (c), the results are shown in Fig. 4. From this figure it follows that the use of equal binary mass transfer coefficients yields a low-temperature solution whereas the use of different binary mass transfer coefficients, resulting in a somewhat higher effective mass transfer coefficient of component A, yields a high-temperature solution. Due to the shape of the profiles these two solutions differ significantly. The high-temperature solution of Fig. 4 will of course not be encountered in practice since vaporization of the solvent will occur. The results presented here are just meant to illustrate the possible effect of small changes of the mass transfer coefficient. However, it should be mentioned that vaporization of the liquid can be taken into account in our transfer model.

In case of the second-order chemical reaction with high solubility of A and low maximum enhancement factor high absorption rates result and consequently heat effects play an important role [see Fig. 3(b)]. It can be seen that the value of Le' influences the maximum absorption rate. In case of $Le' = 10$ components A and B in the solvent will experience the same temperature, whereas in case of $Le' = 1$ A will experience a higher temperature than B, resulting in a different maximum enhancement factor. When using the analytical expressions errors up to 15% can be expected.

Temperature-dependent chemical reaction rate constant

In this case E_D and E_s were set equal to zero, whereas E_{a1} was given a value of 25,000 J/mol. From eq. (9) it can be concluded that the chemical reaction rate constant increases with increasing temperature. As a consequence, in case of an exothermal chemical reaction, the heat production rate due to chemical conversion enhances the chemical reaction rate, resulting in different, often higher, mass transfer rates. The results of the simulations are presented in Figs 5(a)–(d). In order to enable proper comparison, the absorption rates have been plotted as a function of *Ha* evaluated at liquid bulk temperature.

From Fig. 5(a), which shows the results of the second-order chemical reaction in the second composition regime, it can be concluded that for (pseudo) first-order chemical reaction with low solubility of A, a large increase in absorption flux occurs at high values of *Ha* due to heat generation. If the heat effects are neglected large errors will result (i.e. 50% and more). The value of *Le'* has no significant effect on the mass transfer rates and the approximate analytical solution predicts the numerically calculated molar flux of A within 15%.

In case of high solubility of A [see Fig. 5(b)] the analytical results show a sudden increase in $\mathscr{E}$ at $Ha \approx 0.1$. Due to numerical problems the computations could unfortunately not be performed for higher *Ha* values. The explanation for this fact follows from Fig. 6 which shows the heat production rate and heat withdrawal rate as a function of the interface temperature T_i for different k_{01} values in case of equal binary mass transfer coefficients. For low k_{01} values, the heat balance possesses a low-temperature solution, whereas for high k_{01} values ($> 3.10^8$ mol/m^3/s) only a high-temperature solution exists (this latter solution is not shown). The curve also provides the clue to why the numerical problems emerge. The model will try to generate a solution in the low-temperature range, where the heat production curve is at minimum distance to the heat withdrawal curve. Further it is seen that for $k_{01} = 1.10^8$ mol/m^3/s multiple solutions exist, of which the two solutions with the highest temperature are non-existent in practice since vaporization

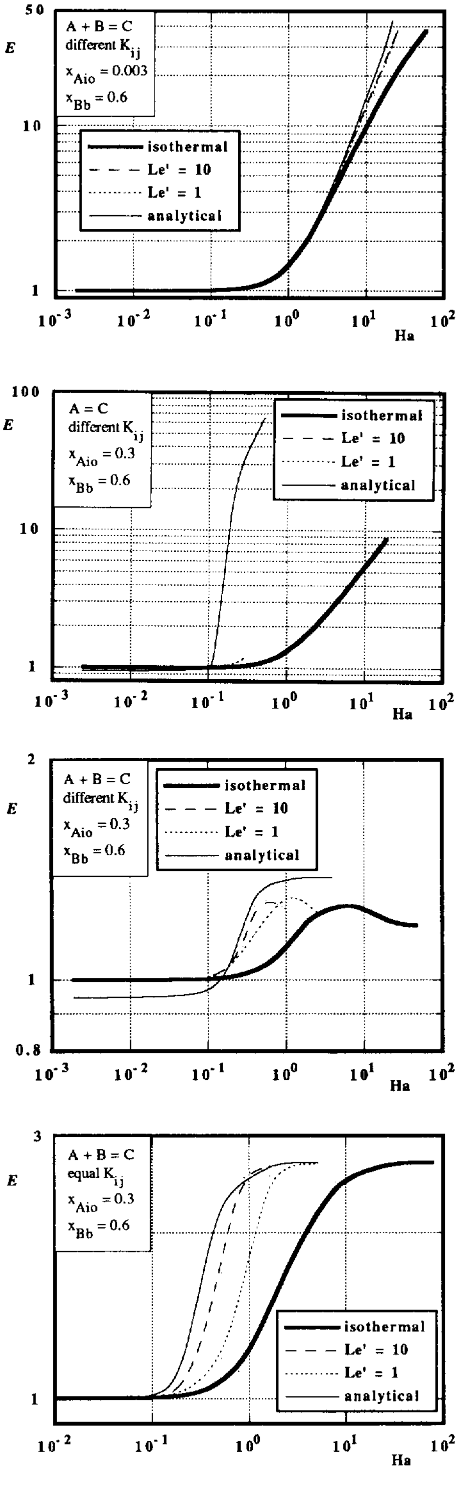

Fig. 5. Dimensionless absorption flux $\mathscr{E}$ of component A obtained from the numerical model and the analytical expressions as a function of the Hatta number in case the chemical reaction rate constant is temperature dependent: (a) second-order chemical reaction, different binary mass transfer coefficients and second composition regime; (b) first-order chemical reaction, different binary mass transfer coefficients and third composition regime; (c) second-order chemical reaction, different binary mass transfer coefficients and third composition regime; (d) second-order chemical reaction, equal binary mass transfer coefficients and third composition regime. Parameter values are given in Table 1.

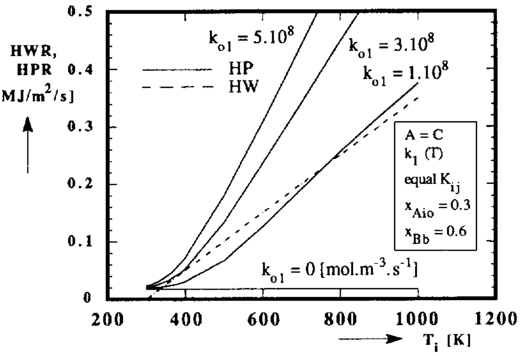

Fig. 6. Heat withdrawal rate (HWR) and heat production rate (HPR) as a function of the interface temperature T_i calculated from the analytical expressions in case of first-order chemical reaction, equal binary mass transfer coefficients and third composition regime for different k_{01} values. Parameter values are given in Table 1.

of the solvent will occur, which has not been accounted for in the present calculations.

Figures 5(c) and (d) show the results for the second-order chemical reaction in case of a high solubility of A for, respectively, different and equal binary mass transfer coefficients. From these figures it can be concluded that enhancement of mass transfer due to heat production occurs at lower *Ha* values in comparison to the isothermal case, but the differences diminish at high *Ha* values. In case of different binary mass transfer coefficients the relative deviation between the results for $Le' = 10$ and the results for $Le' = 1$ is low, due to low maximum enhancement factors, whereas in case of equal binary mass transfer coefficients, this deviation is high for intermediate *Ha* values. The latter is due to the steepness of both curves.

All three parameters are temperature dependent

In this case all activation energies were given nonzero values (see Table 1). This will result in the following three competing effects in case of absorption with associated heat production compared to the isothermal case: decrease in solubility with increasing temperature on one hand and increase in both binary mass transfer coefficients and chemical reaction rate constant with increasing temperature on the other hand.

For a second-order chemical reaction with low solubility and high maximum enhancement factor the results are shown in Fig. 7(a). This figure also represents the results of a first-order chemical reaction with low solubility. From Fig. 7(a) it can be seen that the absorption rates for the non-isothermal case with $Le' = 10$ coincide with the absorption rates for isothermal absorption (differences are smaller than 10%). It can be concluded that the increase in binary mass transfer coefficients and chemical reaction rate constant compensates for the decrease in solubility. The difference between the results for $Le' = 1$ and $Le' = 10$ is smaller than 5%, whereas the approximate analytical expression predicts the numerically calculated absorption rates within 10% accuracy for $Le' = 10$. This error may be due to the increase of the fraction of component C in the liquid film or the use of the approximate expression for N_δ.

In case of high solubility of A [see Fig. 7(b)] the three heat effects do not compensate each other and consequently the overall thermal effect is more pronounced: from Figs 2(b), 3(b) and 5(c) it can be concluded that for $Le' = 10$ and low Hatta number, the heat production changes the absorption rate, respectively, with −60% (temperature-dependent solubility), + 3000% (temperature-dependent mass transfer coefficients) and 0% (temperature-dependent chemical reaction rate constant). Since the overall effect corresponds to a decrease in absorption flux of about 50%, it can be concluded that the individual effects cannot simply be added to obtain the overall effect.

For the second-order chemical reaction it can be seen that the instantaneous regime has not been reached yet due to heat effects and additionally that the absorption fluxes almost equal those of the first-order chemical reaction.

For both reaction schemes the infuence of *Le'* value on the absorption rates is limited to 20% whereas the analytical expression predicts the numerically calculated results within 10%.

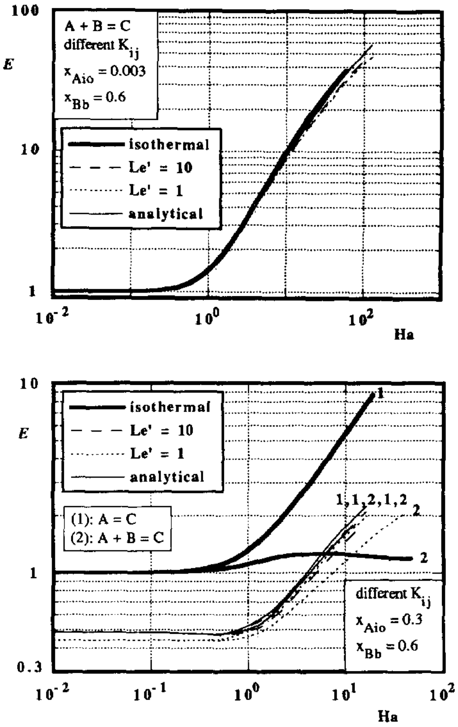

Fig. 7. Dimensionless absorption flux $\mathscr{E}$ of component A obtained from the numerical model and the analytical expressions as a function of the Hatta number in case the solubility, the binary mass transfer coefficients and the chemical reaction rate constant are temperature dependent: (a) second-order chemical reaction, different binary mass transfer coefficients and second composition regime; (b) first-order and second-order chemical reaction, different binary mass transfer coefficients and third composition regime. Parameter values are given in Table 1.

4. DISCUSSION AND CONCLUSIONS

From the results presented in this paper, it is clear that heat effects may play an important role in mass transfer processes with chemical reaction. Heat effects are especially important in those cases where the mass transfer rates are high, due to a high solubility of the absorbed gas or due to a high chemical reaction rate. Evidently the value of the mass transfer rate in a situation in which heat effects should be taken into account will depend on the values of the absorption heat and chemical reaction heat as well as the values of the three, in this paper mentioned, activation energies. Numerical simulations show that, when compared to the corresponding isothermal case, the thermal effects can affect the mass transfer rates by as much as a factor of 30. Due to heat production, three competing effects exist: increase in mass tranfer rate due to increase in binary mass transfer coefficients and increase in chemical reaction rate and decrease in mass transfer rate due to decrease in solubility of the absorbed gas. It may be possible that these three effects compensate each other resulting in a zero change in mass transfer rate in comparison to the isothermal case.

The mass transfer rate under non-isothermal conditions with $Le' = 10$ can be estimated very well from the approximate analytical expressions, presented in this paper. In all cases, which have been studied, the maximum difference amounts to 25%, but in most cases is smaller than 10%. So the analytical solution presented in this paper is very useful to estimate the influence of the heat effects on the mass transfer rates, assuming $Le' = \infty$. In most cases this yields also a reasonable estimate of the mass transfer rate in case $Le' = 1$.

In case of a second-order chemical reaction it was shown that thermal effects may change the maximum enhancement factor and consequently shift the absorption from the instantaneous regime to the pseudo-first-order regime.

From Figs 4 and 6 it followed that multiple solutions of the analytical expressions [eqs (11)–(21)] are possible. The maximum number of solutions is three, of which two will be stable and the intermediate one unstable. Further it was shown that a minor change of the effective mass transfer coefficient of the absorbed species in the liquid mixture or of the chemical reaction rate constant, can cause a significant change in mass transfer rates. A low-temperature solution can change into a high-temperature solution, resulting in completely different mass transfer rates. At these high-temperatures evaporation of the solvent mixture becomes very important. As this has not been taken into account in our calculations, the presented high-temperature solution does not correspond to reality. When heat effects are taken into account evaporation of the liquid mixture should also be taken into account, especially when the calculated interface temperature is near the boiling temperature of the liquid. From the above it is concluded that there may exist non-isothermal gas–liquid absorption systems where minor changes in parameters appearing in the heat balance, e.g. binary mass transfer coefficients, chemical reaction rate constant, Le' number or heat transfer coefficients, may change the system behaviour drastically; It would be very interesting to show this phenomenon experimentally.

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NOTATION

c_T	total concentration, mol/m^3
C_{pi}	heat capacity of component i, J/mol K
d_{ij}	D_{As}/D_{ij}
D_{ij}	binary diffusion coefficient, m^2/s
$\mathscr{E}$	ratio of absorption flux and corresponding isothermal physical absorption flux
E_A	enhancement factor
E_{a1}	activation energy forward reaction, J/mol
E_D	activation energy of diffusion, J/mol
E_s	activation energy of dissolution, J/mol
h_l	heat transfer coefficient, λ/δ_h, J/K s
H_i	partial molar enthalpy of component i, J/mol
ΔH_R	heat of reaction, J/mol
ΔH_s	heat of dissolution, J/mol
Ha	Hatta number as defined in eqs (15) or (18)
k_1	temperature-dependent forward reaction rate constant, mol/m^3 s
k_{01}	forward reaction rate constant, mol/m^3
K_{ij}	binary mass transfer coefficient, D_{ij}/δ_m, m/s
Le'	modified Lewis number, $\delta_{h,l}/\delta_{m,l}$
m_i	solubility of component i, x_i/y_i
N_i	molar flux of component i, mol/m^2 s
$N_{i,0}$	molar flux of component i through gas–liquid interface, mol/m^2 s
$N_{i,\delta}$	molar flux of component i through mass transfer film–bulk interface, mol/m^2 s
R_{gas}	gas constant, J/mol K
R	reaction rate, mol/m^3 s
T	temperature, K
T_i	interface temperature, K
x_i	molar fraction (in liquid phase) of component i
x_{ii}	molar fraction (in liquid phase) of component i at interface
x_{ib}	molar fraction (in liquid phase) of component i in bulk
y_i	molar fraction in gas/vapour phase of component i
z	distance in film, m

Greek letters

α	thermal diffusion coefficient, $\lambda/\rho \cdot C_p$, m^2/s
δ_h	thickness of heat transfer film, m
δ_m	thickness of mass transfer film, m
η	distance in film, z/δ_m
λ	conductivity, J/m K s
ν_i	stoichiometric coefficient of component i (reactant negative, product positive)

Subscripts

A	component A
i	component i
i	interface
l	liquid phase
0	reference state

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