On the Absorption of Isobutene and *trans*-2-Butene in Sulfuric Acid Solutions

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In reactions in which alkenes react in the presence of homogeneous Brønstedt acid catalysts, the protonation step is rate determining. Existing reaction rate correlations for protonation of butenes in sulfuric acid solutions are not consistent and limited to sulfuric acid concentrations below 80 wt %. The absorption of isobutene and *trans*-2-butene in sulfuric acid solutions was studied in the range of 30−98 wt %. Reevaluation of literature data, completed with new data from this study, revealed a set of kinetic rate data which coincide satisfactorily. Experiments and modeling of the absorption experiments showed a strong dependence of the reaction rate on local mixture composition through the activity coefficient of the protonating agent. This strong dependence prevents the occurrence of a diffusion-limited absorption regime. Application of the usually used criteria for operating in the kinetic regime can lead to erroneous results.

1. Introduction

The absorption of alkenes, e.g., butenes, in sulfuric acid solutions is frequently found in large-scale commercial applications. Especially, the removal of isobutene from C_4 streams produced by a naphtha cracker via selective hydration and the production of *sec*-butanol from linear butenes are important industrial applications. In these processes the first reaction step is the formation of a highly reactive intermediate species: the carbocation. In a second step water is added directly to react with the corresponding alcohol or, alternatively, in a second step a hydrogen sulfate ion may be added to form a butyl hydrogen sulfate ester, which can be hydrolyzed to give the corresponding alcohol in an indirect route. For both the direct and indirect hydration path, the protonation step is assumed to be rate determining.

Proton-transfer reactions can be extremely fast; e.g., the second-order forward reaction rate constant for the reaction of a proton and a hydroxide ion to form water was found to be 1.4×10^{11} L/mol·s (Eigen (1963)), which is probably the fastest reaction known in aqueous solution. Comparable rates are, e.g., found in the case of dissolving acid gases such as HCN and H_2S in water. For "diffusion-controlled" reactions of nonionic species, the "rate constant" for bimolecular reactions is estimated to be 8×10^9 mol/L·s for reactions in water. In other solvents this value will decrease with increasing solvent viscosity. However, for the protonation of unsaturated hydrocarbons, the experimentally found reaction rates are much lower than those for the cases mentioned above.

Since the 1940s, considerable attention has been paid to the mechanism and kinetics of the protonation reaction of olefins in (strong) acid solutions. However, when the literature results on the reaction kinetics are summarized, it can be concluded that, especially for 2-butenes, no consistency exists for the observed dependency of the kinetic rate constants on acid strength for the protonation of butenes in sulfuric acid solutions (Figure 1). Moreover, no data are available for experiments in sulfuric acid solutions of 80 wt % and more, which are typical concentrations used for, e.g., the Koch reaction and alkylation reactions.

Because of the observed discrepancy between the data presented in literature and because of the lack of information for highly concentrated acid solutions, an experimental study of the absorption kinetics over the range of 30−96 wt % sulfuric acid solutions was carried out to study the reaction kinetics of the protonation step. Since concentrated acid solutions are thermodynamically highly nonideal, it seems appropriate to base the reaction rate expression on activities instead of concentrations of the reactants. Among others, Pohorecki and Moniuk (1988) have shown that the reaction rate for the reaction of a hydroxide ion with dissolved carbon dioxide is strongly influenced by the ionic strength of the solution. Moreover, Engel et al. (1995) have demonstrated that a very good correlation of experimental data for the hydrogenation of bicarbonate to formic acid and vice versa is obtained by using a kinetic relation based on activities.

As the major part of the literature data were obtained by absorption experiments and since it is shown that the absorption is substantially affected by the acid strength, the reactive absorption process is also studied theoretically in order to exclude possible disturbing influences of mass-transfer limitations.

2. Reaction Mechanism and Kinetics

During the absorption of butenes in sulfuric acid solutions, several reaction products can be formed, including alcohols, esters with sulfuric acid, ethers, sulfonic acids, oligomerization, and cracking products (Robey (1941)). The variety of reaction products formed depends severely on the butene used, acid strength, local mixing conditions, and temperature. From the literature it can be concluded that these reactions proceed via the initial formation of a carbocation. This initial reaction step is generally assumed to be rate determining. Irrespective of the reactions following this initial step, the protonation kinetics can, under certain conditions, be determined from butene absorption kinetics.

2.1. Reaction Mechanism. The mechanism of protonation reactions in homogeneous Brønstedt acid solutions has been discussed several times in literature. It can be concluded that no agreement exists on the exact mechanism. So far, the mechanism is claimed to proceed either via an A-1 or via an A-S_E2 mechanism. The A-1 mechanism was proposed for the protonation

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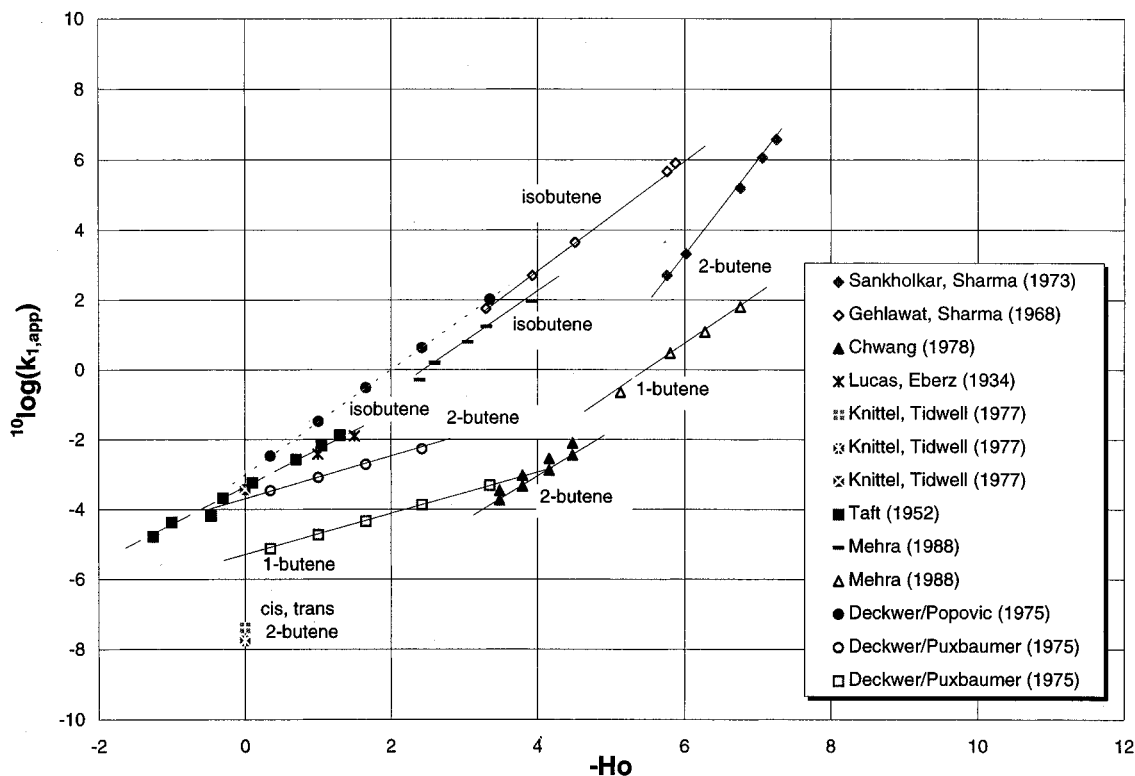
Figure 1. Apparent kinetic rate constants for the butene absorption in sulfuric acid solutions as reported in literature.

of isobutene by Taft (1952). In this mechanism no water is included in the transition state of the rate-determining step, which was supported by a low entropy of activation for the hydration of isobutene.

Among others, Kresge et al. (1971) suggest that the protonation mechanism for simple olefins is the A-S_E2 mechanism. This suggestion is supported by experiments in which general acid catalysis was observed for the protonation of 2,3-dimethyl-2-butene and *trans*-cyclooctene.

For both the A-1 and the A-S_E2 mechanism, it can be derived that, assuming elementary reaction steps, the reaction rate will be first order for the butene used and the proton(ating species), respectively.

In literature the protonation reaction rate was found to be first order in the butene concentration in all cases.

2.2. Reaction Kinetics. As concluded in section 2.1, the rate-determining step for the hydration of olefins is the formation of an intermediate carbocation from the olefin and a proton or a proton-donating compound. In describing reaction kinetics usually power-law reaction rate expressions are applied, based on the concentrations of the reactants involved. Considering the very pronounced dependency of the kinetics of protonation reactions on acid strength, the thermodynamic nonideality of the acid solutions is probably the most important factor affecting the reaction kinetics. Several studies (e.g., Pohorecki and Moniuk (1988), Engel et al. (1995)) have shown that the conversion of concentration-based reaction rate equations to activity-based reaction rate equations reduced the scatter in correlating experimental data considerably for the thermodynamically nonideal gas absorption processes.

This was also already recognized by Taft (1952), who found that describing the hydration kinetics for isobutene in aqueous nitric acid solutions with rate expressions using the concentrations of the reacting species (butene concentration, c_B, and acid concentration, c_A, respectively) only leads to acceptable results for very dilute

acid solutions. Taft correlated his kinetic rate data successfully to the Hammett acidity function Ho for the acid solutions. Since the Hammett acidity function is an indicator for the protonating activity of the acid solution, this can be considered a first approximation to correct for the thermodynamic nonideality of the solution.

Since the early work of Hammett and Deyrup (1932), proton activities are generally indicated using a proton activity scale, determined experimentally by measuring the extent of ionization of inert, weak indicator bases with a well-known ionization constant. The originally proposed Hammett cancellation assumption was shown to be invalid, and more than 100 different acidity scales have been developed and tabulated, of which the original Hammett acidity function (Ho), based on nitroaniline indicators, is most commonly used. Attempts to derive a more general acidity function, e.g., the excess acidity function and the Bunnett–Olson method (Cox and Yates (1987)), supported by the observation that the different acidity scales approximately show a mutual linear dependency, have been developed, but this has not led to a generally accepted result yet.

In this work an elementary bimolecular reaction is assumed between the butene and an acid compound (a proton or a proton donor). It is proposed that the reaction kinetics can be described using a reaction rate expression based on the activities of the reactants in the reaction mentioned above. In this case (which corresponds with an A-S_E2 mechanism) the rate expression becomes

$$-R_B = k_T a_B a_{H+} = k_T \gamma_B \gamma_{H+} c_B c_{H+} = k_h^* a_{H+} c_B = k_{1,app} c_B \quad (1)$$

In this expression k_T represents the intrinsic kinetic rate constant, which no longer depends on acid concentration. The apparent first-order reaction rate constant $k_{1,app} = k_T a_{H+} \gamma_B$ thus depends linearly on the proton

Table 1. Rate Expressions for Hydration of Simple Olefins in Aqueous Acid Solutions

alkene	wt % H_2SO_4	T [K]	log $k_{1,app}$ = $k_{1,app}$ [1/s]	method[a]	ref
ethylene	78−88	298	−1.54Ho−14.8	1	Chwang et al., 1977
propylene	48−60	298	−1.39Ho−8.62	1	Chwang et al., 1977
1-butene	30−50	303	−0.55Ho−4.5	2	Deckwer et al., 1975
2-butenes	25−60	303	−0.55Ho−3.5	2	Deckwer et al., 1975 (I)
cis-2-butene	48−58	298	−1.49Ho−8.34	1	Chwang and Tidwell, 1978
trans-2-butene	48−58	298	−1.40Ho−8.35	1	Chwang and Tidwell, 1978
2-butenes	70−80	301	−2.05Ho−10.8	3	Sankholkar and Sharma, 1973
isobutene	49−70	303	−1.60Ho−3.6	4	Gehlawat and Sharma, 1968
isobutene	10−50	303	−1.50Ho−3.0	5	Deckwer et al., 1975 (II)
isobutene	0.1−1.5 M HNO_3 soln.	298	−1.10Ho−1.55	6	Taft, 1952
2-methyl-2-butene	61−75	301	−1.49Ho−1.31	3	Sankholkar and Sharma, 1973
3-hexene (E)	48−58	298	−1.39Ho−7.96	1	Chwang and Tidwell, 1978
3-hexene (Z)	48−58	298	−1.35Ho−7.89	1	Chwang and Tidwell, 1978
cyclohexene	45−57	298	−1.28Ho−7.35	1	Chwang et al., 1977

[a] Methods used are as follows: 1, slow reaction regimes (homogeneous liquid-phase reaction), UV detection method; 2, reaction in the transition regime: homogeneous liquid phase reaction to ... (method 3); 3, pseudo-first-order reaction regime ($E = Ha$) using a stirred cell apparatus; 4, pseudo-first-order reaction regime ($E = Ha$) using a laminar jet apparatus; 5, reaction in the slow and transition reaction regime, using a bubble column; 6, slow reaction regimes (homogeneous reaction), where pressure decrease is measured.

activity and the activity coefficient of butene in the solution. Note that assuming an A-1 mechanism would lead to the same overall equations.

The apparent first-order rate constant $k_{1,app}$ is often found to be proportional to the Hammett acidity function Ho (see Table 1):

$$\log k_{1,app} \propto -Ho \qquad (2)$$

This result is consistent with the derivation given above, since $-Ho \propto \log(a_{H^+})$.

In Table 1 the reaction rate expressions found in literature are summarized. From Table 1 and Figure 1, it can be concluded that the kinetic rate data reported in literature do not yield a consistent set of data for the observed dependency of the kinetic rate constants for the protonation of butenes in sulfuric acid solutions on acid strength. At high and low acid strength the protonation of trans-2-butene seems to become faster than the protonation of isobutene, which is rather unrealistic since a secondary instead of the more stable tertiary carbocation must be formed.

3. Theory

In gas absorption in which gas−liquid mass transfer is accompanied by a chemical reaction in the liquid phase, the gas absorption rate may be enhanced significantly. Generally, for describing this effect the enhancement factor concept is applied, in which the enhancement factor, E, is defined as the ratio of the specific rate of gas absorption in a reactive liquid to the specific rate of absorption under identical conditions in a nonreactive liquid (physical mass transfer). Due to the importance of this enhancement factor for design purposes, several theoretical models have been developed to calculate this effect. Well-known and frequently used one-parameter models are the film model, the Higbie penetration model, and the Danckwerts surface renewal model. For several (asymptotic) cases analytical expressions have been derived for irreversible reaction kinetics, based on concentration-based power law reaction kinetics (van Krevelen and Hoftijzer (1948), Hikita and Asai (1963), DeCoursey (1974)). A review of the approximate analytical solutions and numerical models for reversible reactions is given by van Swaaij and Versteeg (1992). The model equations derived for the description of absorption of olefins in acid solutions were solved numerically, using numerical techniques identical with those applied by Versteeg et al. (1989).

The absorption of butenes in sulfuric acid solutions, accompanied by the protonation reaction can be represented as follows:

$$C_4H_8(G) + H^+(L) \leftrightarrow C_4H_9^+(L) \leftrightarrow products(L)$$

In this theoretical part the experimental conditions of the absorption experiments are analyzed to assure that mass-transfer limitations do not occur. In the experiments ambient temperature and moderately to highly concentrated fresh acid solutions are applied, and the product loading of the solution at the end of the experiments is low (<0.01 M). Considering that under these conditions neither isobutene nor tert-butanol can be extracted from the acid solution with inert solvents, it seems justified that a proton is bonded to the reaction products. The reaction can then be considered irreversible. Thus, the concentration-based equilibrium constant for the protonation reaction was chosen rather high ($K_{eq,c} = 10^9$ L/mol). Schematically, the reaction system, as it was implemented in the absorption model, is simplified to

$$B(G) + A(L) \rightleftharpoons C(L)$$
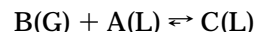
In section 2.2 it was concluded that the reaction rate expression should be based on activities, in accordance with existing kinetic correlations for the isobutene−sulfuric acid reaction system.

3.1. Model Equations. In this study the processes of mass transfer accompanied by chemical reaction during gas absorption are modeled for the penetration theory of Higbie for the chemical system of the present work. The mass balance for each species is given by eq 3. Initially, the liquid phase only contains liquid-phase

$$\frac{\partial c_i(x,t)}{\partial t} = D_i \frac{\partial c_i^2}{\partial x^2} + R_i \qquad \text{with } i = A, B, C \qquad (3)$$

reactant A ($a$cid) and contains no dissolved gas-phase reactant B ($b$utene) or product C.

I.C. $t = 0$ $\forall x$ $c_i(x,t) = 0$ $(i = B, C)$

$$c_A(x,t) = c_A^{bulk}$$

The boundary conditions at the gas−liquid interface were obtained by assuming that A and C are nonvolatile and by implementing continuity of mass flux for com-

ponent B at the gas–liquid interface.

B.C. $x = 0$ $t > 0$

$$-D_B \frac{\partial c_B(0,t)}{\partial x} = k_{g,B}\left(c_{B,g} - \frac{He_B c_B(0,t)}{RT}\right)$$

$$-D_i \frac{\partial c_i(0,t)}{\partial x} = 0 \quad (i = \text{nonvolatile components A, C})$$

Since the loading of the liquid phase is negligible during the absorption experiments, no significant variations of the liquid bulk phase composition occur. Therefore, no material balance over the liquid bulk phase is required.

$x = \infty$ $(t > 0)$

$$c_i(x,t) = c_{i,\text{bulk}} = 0 (i = \text{B, C})$$

$$c_A(x,t) = c_A{}^{\text{bulk}}$$

The reaction rate terms $R_A(x,t) = R_B(x,t) = -R_C(x,t)$ are assumed to be first order toward the butene activity (a_B) and first order toward proton activity (a_A), as given in eq 1*.

$$-R_B(x,t) = k_T[a_B a_A]_{(x,t)} = k_T[\gamma_B \gamma_A c_B c_A]_{(x,t)} = [k_h{}^* a_A c_B]_{(x,t)} = [k_{1,\text{app}} c_B]_{(x,t)} \quad (1^*)$$

From previous studies it was often found that $\log k_{1,\text{app}} = a(-Ho) + b$, as can be seen in Table 1. With eq 1* the reaction rate expression becomes

$$-R_B(x,t) = k_T[\gamma_A \gamma_B c_A c_B]_{(x,t)} = 10^{a\{-Ho(x,t)\}+b} c_B(x,t) \quad (4)$$

With this, an expression for the product of the concentration-based activity coefficients can be derived:

$$(\gamma_A \gamma_B)_{(x,t)} = \frac{10^{a(-Ho(x,t))+b}}{k_T c_A(x,t)} \quad (5)$$

Since the sparingly soluble gas-phase component is assumed to have no influence on the local acidity, $-Ho$ and ($\gamma_A \gamma_B$) will be a unique function of the local acid concentration c_A. At infinite dilution ($c_A \rightarrow 0$) the acid concentration will be determined by the water dissociation equilibrium.

Writing eq 1* as $-R_B(x,t) = k_T[\gamma_B \gamma_A c_B c_A]_{(x,t)} = k^\#(x,t)[c_B c_A]_{(x,t)}$ yields an expression which is very similar to the one for the well-known situation of gas absorption followed by a bimolecular irreversible chemical reaction $-R_B(x,t) = k_{1,1}[c_B c_A]_{(x,t)}$. The major difference is the apparent kinetic rate constant, $k^\#(x,t)$, which now strongly depends on the local liquid-phase composition.

In this theoretical study the diffusion process is described using Fick's law, and in most of the calculations all diffusion coefficients are taken equal and constant. Considering the nonideality of the liquid phase, it would be appropriate to incorporate the effect of an activity gradient on the diffusion process. For binary systems the effect of an activity gradient can be described using a thermodynamic correction factor: $D_i = D_{i,0}\Gamma_i = D_{i,0}(1 + x_i \, d\{\ln \gamma_i\}/dx_i)$.

Since no reliable activity models are available for the concentrated sulfuric acid solutions, the effect was approximated by treating sulfuric acid solutions as a binary mixture of water and the protonating agent sulfuric acid. The acid activity coefficient γ_A is now defined according to eq 5*.

$$\gamma_A = \frac{10^{a(-Ho)+b}}{k_h{}^* x_A} \quad (5^*)$$

Using this approximation, the thermodynamic correction factor $\Gamma_A = (1 + x_A \, d\{\ln \gamma_A\}/dx_A)$ is found to be approximately constant (10–15) for mole fractions of $H_2SO_4 > 0.15$ (>50 wt %). For a few cases this thermodynamic correction factor for the diffusion coefficient of the liquid-phase reactant was implemented to study its effect.

The impact of the activity-based reaction rate equation on the reactive absorption process has been studied by performing two types of simulations at identical bulk phase compositions: one for the activity-based rate equation, using the reaction rate expression given in eq 6-a, and one for the concentration-based rate, given in eq 6-b. In the first case the apparent second-order rate

case I: $-R_B = k_T \gamma_A \gamma_B c_A c_B = 10^{a(-Ho)+b} c_B$ with

$$\gamma_A \gamma_B = \frac{10^{a(-Ho(c_A))b}}{k_h{}^0 c_A} \quad \text{(varies with local } c_A\text{)} \quad (6\text{-}a)$$

case II: $-R_B = k^\# c_B c_A$ with

$$k^\# = \frac{10^{a(-Ho)+b}}{(c_A)_{\text{bulk}}} = \text{constant} \quad (6\text{-}b)$$

coefficient $k_T \gamma_A \gamma_B$ varies strongly with local-liquid phase compositions, whereas in the latter case this rate coefficient is constant. In absence of mass-transfer limitations both rate expressions will yield the same result.

3.2. Results. In the simulations where the effect of the activity-based reaction rate equation is studied, in fact only the value of the a-parameter in the $-Ho-\log k_{1,\text{app}}$ correlation is relevant. This parameter solely represents the dependency of the local activity coefficients product on the local acid concentration. From Table 1 it is clear that this parameter varies in a rather narrow range. A value of 1.4 was selected for the simulations. In the simulations presented here the diffusion coefficients of the components A and B were taken equal, unless stated otherwise. The Hatta number was varied in this study via the reaction rate constants k_T (eq 6-a) and $k^\#$ (eq 6-b).

In Figure 2 the enhancement factors, E_B, for the absorption flux of gas-phase component B calculated are plotted versus the Hatta number for reactant B. The Hatta numbers are calculated using liquid bulk phase conditions for the acid concentration c_A. For case II, the open symbols in Figure 2, it is clear that at higher Hatta numbers the enhancement factor is no longer determined by reaction kinetics but by diffusional mass transfer. This is the so-called instantaneous reaction regime, which is characterized by the infinite enhancement factor for irreversible reactions (Westerterp et al. (1984)):

$$E_{B,\infty} = \sqrt{\frac{D_B}{D_A}}\left(1 + \frac{D_A c_{A,\text{bulk}}}{D_B c_B{}^i}\right) \quad (7)$$

For case II the E_B-Ha_B curves can be predicted by the approximate solution methods for irreversible bimolecular reactions mentioned before. For the activity-based reaction rate equation (case I), the calculated enhancement factors differ significantly from the curves obtained for case II. In bimolecular reaction systems
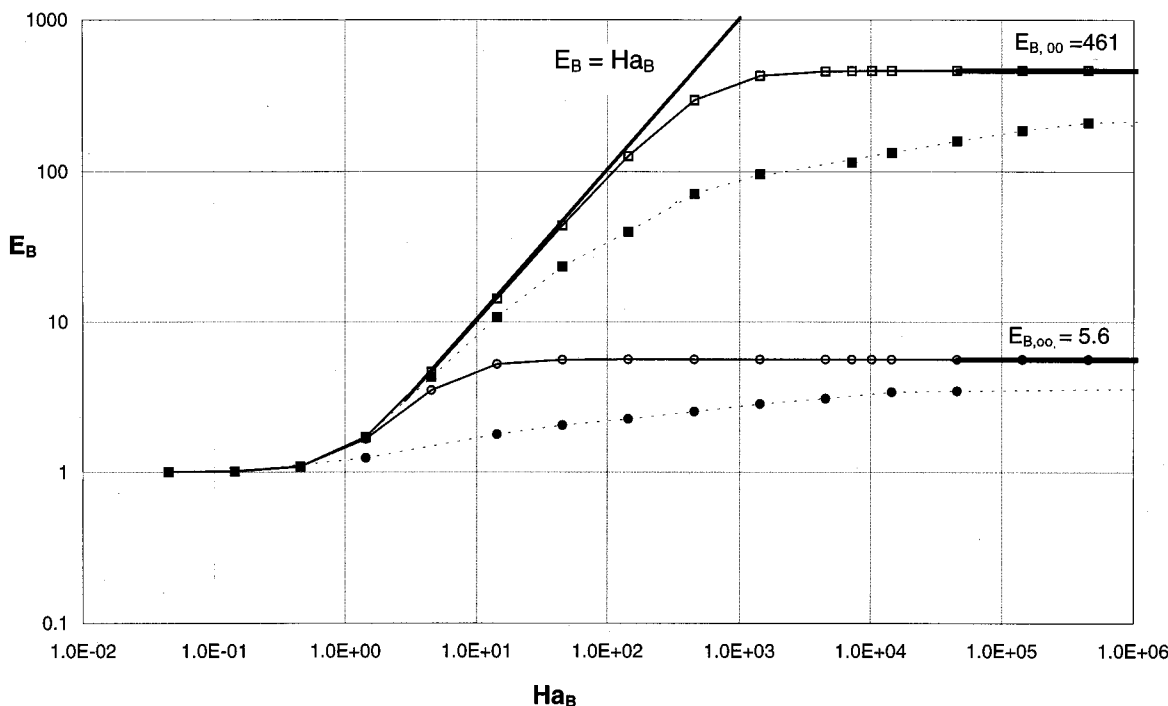
Figure 2. Enhancement factor vs Ha number for gas-phase component B. Open symbols, solid lines: concentration-based reaction rate equation. Closed symbols, dashed lines: activity-based reaction rate equation.

for which an activity-based reaction rate expression applies, the enhancement factors can therefore not be predicted from approximate or analytical solutions for irreversible bimolecular reactions. Two important effects can be distinguished from Figure 2.

First, it is clear that at high values for Ha_B the infinite enhancement factor calculated according to eq 7 is not reached (yet), not even for cases in which the kinetic rate constant is increased to values which are in order of magnitude of rate constants for diffusion-controlled reactions in this system (10^9 L/mol·s and higher). It can be concluded that for this reaction system the infinite enhancement factor cannot be reached.

A second conclusion is of direct practical importance for interpreting experimentally determined absorption fluxes in order to obtain kinetic rate constants. In standard chemical engineering textbooks it can be found that kinetic absorption experiments for fast, bimolecular gas−liquid reactions should be carried out in the fast pseudo-first-order regime (Westerterp et al. (1984)). For this regime the experimentally determined enhancement E_B equals the Hatta number. This line, $E_B = Ha_B$, is plotted in Figure 2. It can be seen from Figure 2 that the experimental operating window for kinetic experiments is significantly smaller for the system with the activity-based rate equation; the dashed lines deviate at significantly lower Ha_B values from the $E_B = Ha_B$ line ($Ha_B/E_{B,\infty} < 0.01$).

Parts a−d of Figure 3 clearly show the difference in concentration profiles found for the components A and B in cases I and II near the gas−liquid interface at the end of the contact time. Whereas for case II the instantaneous regime is reached for $Ha_B/E_{B,\infty} > 20$, depletion of B near the gas−liquid hardly occurs in the case of the activity-based rate expression at identical bulk phase conditions.

One may expect from these concentration profiles that the enhancement factor for case I may exceed the enhancement factor for case II, since there is less depletion of component A. However, this is not true! From Figure 2 it is found that the enhancement factor

for case I is significantly lower than the enhancement factor for case II. This can be explained by considering the activity profiles instead of the concentration profiles of component A near the gas-liquid interface.

In Figure 4a,b generalized curves are created for both the irreversible bimolecular (1,1) reaction (case II) and for the reaction rate equation based on activities (case I). In these plots the Hatta number and the enhancement factors are scaled to the infinite enhancement factor as calculated by eq 7 for bulk liquid-phase conditions.

These generalized curves seem valid (within a few percent accuracy) for not too low values of the infinite enhancement factor ($E_{B,\infty} > 10$). This result is not surprising for case II, considering the approximate analytical solutions mentioned. For case I, however, it also seems possible to create such a generalized curve for the reaction system considered.

In constructing Figure 4b, $E_{B,\infty}$ was calculated using eq 7 and varied by changing the concentration of B at the gas−liquid interface, c_B^i. Again it is clear that even for large ratios of $Ha_B/E_{B,\infty}$ ($>10^5$) the infinite enhancement factor will not be reached.

In a few simulations the diffusion coefficient of the acid was increased by factors of 10 and 100 to account for the effect of the nonideality of the acid solution on the diffusion process, as explained in section 3.1. As expected, the operating regime is enlarged since D_A directly influences the infinite enhancement factor according to eq 7. Calculated enhancements did follow the generalized curve presented in Figure 4b.

4. Experimental Work

The absorption experiments in the slow reaction regime were carried out using an intensely stirred gas−liquid reactor, equipped with a gas-inducing stirrer. The reactor used was operated batchwise for the gas phase and the liquid phase (full batch experiment).

The experiments in the fast pseudo-first-order regime ($E_B = Ha_B$, $Ha_B > 3$, and $Ha_B/E_{B,\infty} < 0.01$; see section 3)
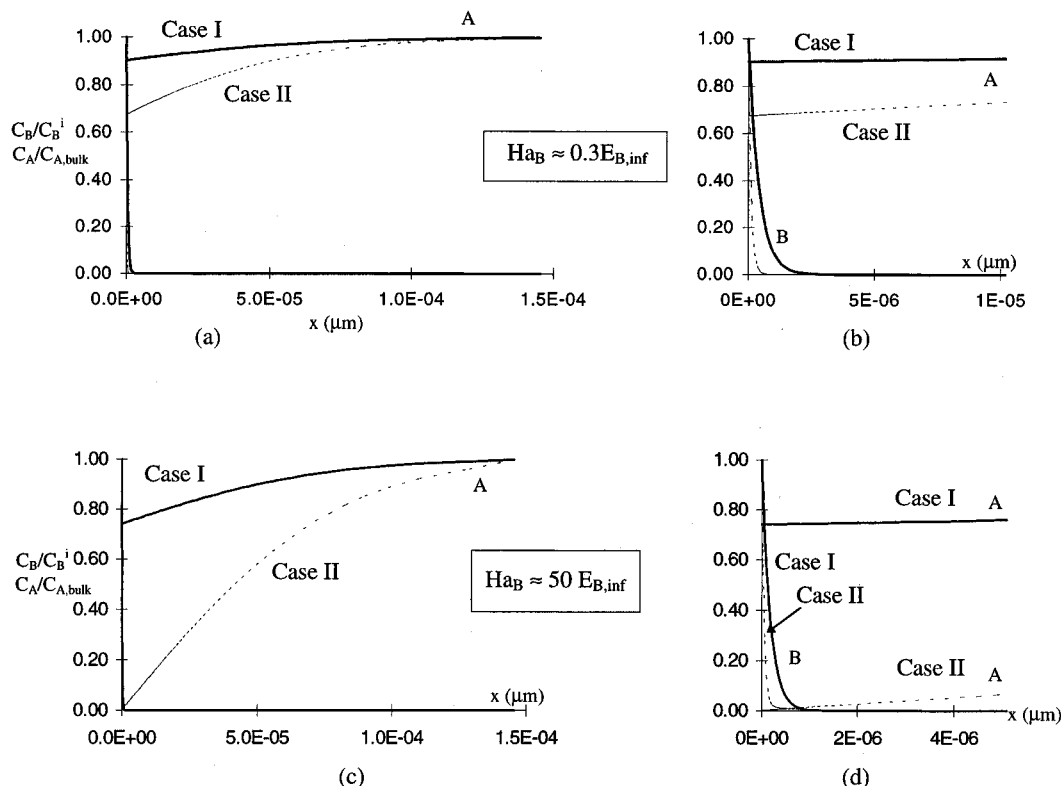
Figure 3. Concentration profile components B (gas phase) and A (liquid phase) in the mass-transfer zone near the gas−liquid interface. In parts b and d the region at the gas−liquid interface is presented in more detail. $E_{B,\infty}$ is calculated according to eq 7. Case I: activity-based reaction rate equation. Case II: concentration-based reaction rate equation.

were carried out in a stirred-cell contactor with a flat interface. The stirred-cell setup (Figure 5) was operated using the liquid phase loaded batchwise in all experiments. The gas phase was used batchwise (at low fluxes) and semibatchwise at high absorption rates. In the full-batch experiments the absorption rate was registered from pressure drop versus time in the stirred cell using a personal computer for data acquisition. In the (gas-phase) semibatch mode the reactor pressure was kept constant at an operating pressure in the range of 5−1000 mbar ($\pm$0.3 mbar), using a PID controller reading the actual reactor pressure from a sensitive pressure indicator and regulating the gas-phase mass flow to the stirred cell through a mass flow controller. The temperature of the (bulk) liquid phase was kept constant at 293.15 K ($\pm$0.1 K). Absorption rates were determined by registering the pressure drop vs time in the gas-phase storage vessel.

For the gas phase the assumption of ideal gas-phase behavior is valid for the semibatch experiments at partial pressures below 5×10^4 Pa. For batch experiments in the slow reaction regime (at approximately 0.9 bar) the nonideal behavior of the gas phase was taken into account. The change of the compressibility factor z in $PV = zRT$ could safely be neglected over the pressure drop during the experiment.

From mass balances for the gas and liquid phases the absorption flux can be related to the intrinsic reaction kinetics. The equations used for P_B−t data interpretation are listed in Table 2.

The experimental procedures were tested successfully, and the setups were characterized by physical absorption experiments of carbon dioxide and butenes in water and measurement of the reaction kinetics for carbon dioxide absorption in alkanolamine solutions. From these experiments it was concluded that kinetic absorption experiments could be carried out (Brilman (1998)).

Chemicals. Acid solutions of different strengths were composed from 96 wt % pro analyses of sulfuric acid (Merck) and demineralized water. Acid strength was determined accurately using a standard NaOH titration method with a Mettler DL25 titrator. For the experiments freshly prepared (unloaded) acid solutions were used, since the presence of butanol will influence both the solution acidity as well as the butene solubility (Friedrich et al. (1981, 1984)). *trans*-2-Butene (quality 1.5) and isobutene (quality 2.3) were purchased from Praxair. Impurities in *trans*-2-butene consist merely of isobutene (2.5%) and butanes (2.0%). Since the absorption of isobutene is much faster (about a factor 1000) than that of *trans*-2-butene, only full-batch experiments were performed with *trans*-2-butene. The initial rapid decrease of the reactor pressure was attributed to the presence of isobutene and was quantitatively in line with the initial amount of the isobutene in the gas phase and experimentally determined specific absorption rates for isobutene under the reaction conditions involved.

5. Physicochemical Parameters

Since sulfuric acid solutions are highly nonideal and the protonation of butenes is relatively fast, physicochemical parameters as the diffusion coefficient and the solubility of butenes in sulfuric acid solutions are difficult to obtain experimentally. An (iso-)butane−(iso)butene analogy is therefore proposed, similar to the well-known N_2O−CO_2 analogy applied for estimating CO_2 solubility and diffusivity in aqueous alkanolamine solutions (Laddha et al., 1981).

Solubility. The solubility of gaseous butenes in sulfuric acid solutions can be determined directly from experiments in the case of absorption experiments in the slow reaction regime ($Ha < 0.2$) from the initial
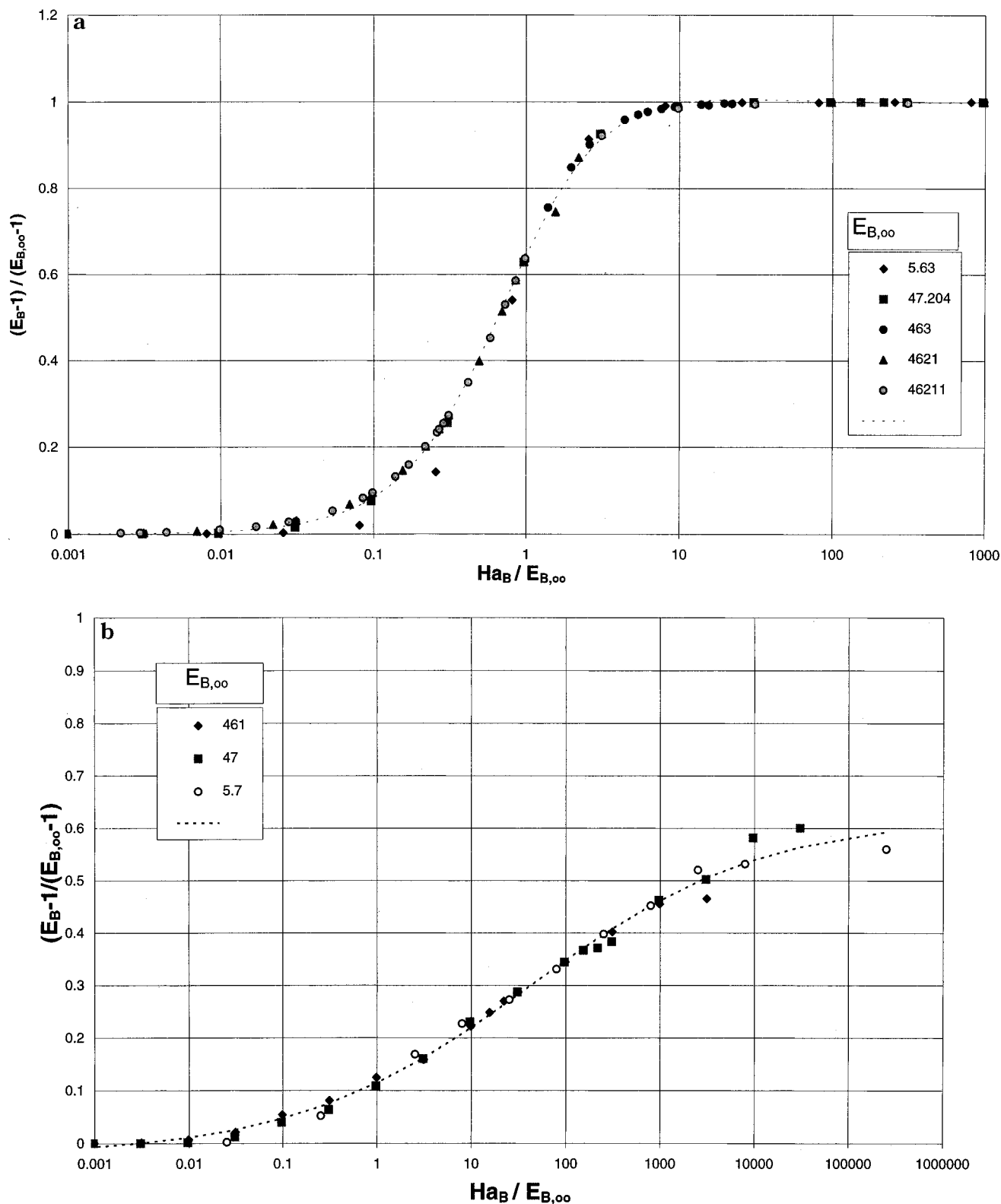
Figure 4. (a) Generalized curve for (1,1) reactions with a concentration-based reaction rate expression. (b) Generalized curve for reactions with an activity-based reaction rate expression. $E_{B,\infty}$ is calculated according to eq 7.

pressure decrease in the batch reactor or by the bromide–bromate method (Lucas and Eberz, 1934). At higher acid concentrations direct measurement of butene solubility is no longer possible.

At low acid concentrations a common salting-out behavior is found for most substances in aqueous sulfuric acid solutions. At higher acid concentrations (from 30 wt %) the Setchenow equation does not hold any longer and salting-out is overestimated by a Setchenow equa-

tion (Friedrich et al. (1981)). Moreover, at higher acid concentrations (>50 wt %), even salting-in will occur. This effect was recognized by several authors (Friedrich et al. (1981), Sanders (1985)).

Rudakov et al. (1989) proposed a correlation for estimating the solubility of gaseous components in aqueous sulfuric acid solutions of 0–100 wt %. This correlation, based on experimental data for nine inert components including isobutane, isopentane, cyclopen-
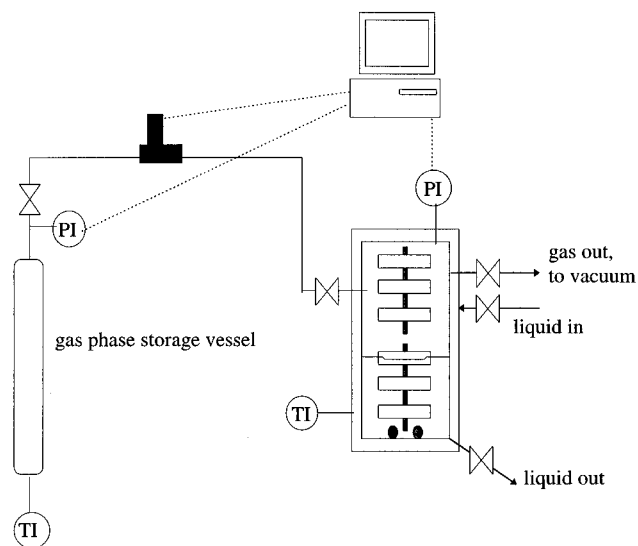
Figure 5. Setup with a stirred-cell apparatus (total volume 1050 mL, $S = 71.0$ cm²).

tane, and methane, was used to estimate the isobutene and *trans*-2-butene solubility in sulfuric acid solutions of different strength. For additional, more detailed information the reader is referred to Brilman (1998).

Diffusion Coefficient. The liquid-phase diffusion coefficient of gaseous solutes in electrolyte solutions strongly depends on the liquid-phase viscosity. For a large number of electrolyte solutions, the experimentally determined Fick diffusion coefficients of several gases can be reasonably correlated (at constant temperature) to viscosity by a modified Stokes–Einstein equation:

$$D\eta^{0.6} = \text{constant} \qquad (8)$$

This correlation was tested for CO_2 in sulfuric acid solutions (Brilman (1998)). Up to 84 wt % eq 8 seems to hold. At higher acid strengths (86, 90, and 96 wt %) the diffusion coefficient of CO_2 was approximately constant at 0.2×10^{-9} m²/s. For butenes the same ratio $D/D_{\text{H2O}} = 0.1$ was assumed in this range.

6. Absorption Experiments

6.1. Absorption of Isobutene. The absorption of isobutene in sulfuric acid solutions was studied in the range 30–98 wt % sulfuric acid, using the stirred-cell setup. The absorption fluxes were independent of the stirrer speed, which was varied over the range 30–66 rpm (k_L increases approximately with 40%). The standard deviation for the absorption fluxes was usually within 5%, except for the experiments at 96 wt % where the standard deviation was 20%. The reaction is apparently first order in isobutene, since the specific rate of absorption was found to be proportional to the partial pressure of isobutene. This result is in accordance with previous studies of Taft (1952) and Gehlawat and Sharma (1968).

Derivation of the kinetic rate constants from absorption fluxes introduces some uncertainties with respect to the physicochemical data used (solubility, diffusivity). For comparison with literature data it is therefore more appropriate to compare directly the absorption fluxes. The obtained absorption fluxes coincide with the existing data of Gehlawat and Sharma (1968) (see Figure 6). The experimentally determined specific absorption fluxes are reported in Table 3.

In the estimation of the physicochemical parameters the possible errors made, though probably up to 100% for solubility and diffusivity, are small with respect to the variation of the calculated kinetic rate constants with changing acid strength ($k_{1,\text{app}}$ varies over more than 10 decades!). Using the isobutane–isobutene analogy for the interpretation of the flux data of Gehlawat and Sharma (1968), together with additional flux data determined in this study, and incorporating data of other authors for the homogeneous reaction regime, a fairly good correlation of kinetic rate constants with the Hammett acidity function is obtained, as can be seen in Figure 7, using the following correlation:

$$\log k_{1,\text{app}} = a(-Ho) + b$$

The kinetic rate constants thus determined in the enhanced mass-transfer regime are found to be consistent with data, available from literature, for the slow reaction regime (homogeneous liquid-phase reaction). The best overall correlation for $k_{1,\text{app}}$ at 293 K is given by eq 9.

$$\log k_{1,\text{app}} = -1.35Ho - 3.3 \qquad (9)$$

6.2. Absorption of *trans*-2-Butene. The protonation of *trans*-2-butene was studied in the slow reaction regime ($Ha_B < 0.2$) and in the fast pseudo-first-order reaction regime ($Ha_B > 2$). The intensely stirred tank reactor could be operated in the slow reaction regime for acid concentrations up to 60% sulfuric acid. The rate of *trans*-2-butene absorption was found to depend linearly on the butene partial pressure. From the initial pressure drop in each experiment the solubility of *trans*-2-butene under the reaction conditions was determined with an accuracy of 5%. The experiments in the stirred-cell setup at acid concentrations of more than 70 wt % sulfuric acid showed that the specific rate of absorption was independent of the stirring speed which was varied within the range 30–80 rpm. Experimentally determined absorption fluxes for the fast reaction regime and estimated kinetic rate constants for the slow reaction regime are listed in Table 4. The standard deviation for the absorption fluxes is less than 5%.

The absorption fluxes of Sankholkar and Sharma (1973) are not completely consistent with the present data, possibly due to the fact that Sankholkar and Sharma produced their own butenes, in which some isobutene may have been present which is much faster reacting, by dehydration of *sec*-butylalcohol.

Experimental data from this work for the homogeneous regime as well as for the fast pseudo-first-order regime ($E_A = Ha_A$) could be correlated fairly well with the Hammett acidity function (Figure 8).

These data are in accordance with data of Knittel and Tidwell (1977), Chwang and Tidwell (1978), and Mehra et al. (1988). The data do not confirm the measurements by Deckwer and Puxbaumer (1975). Considering the relatively short measurement times applied by Deckwer and Puxbaumer, the deviating results are probably caused by the presence of a minor amount of isobutylene in the 1- and 2-butenes used. Their data set seems in conflict with most other data available in literature (Figure 1) and was therefore left out of Figure 8. The overall correlation for $k_{1,\text{app}}$ (at 293 K) is found to be

$$\log k_{1,\text{app}} = -1.5Ho - 9.0 \qquad (10)$$

Table 2. Time−Pressure Correlations for Interpretation of Absorption Fluxes[a]

reaction regime	criteria	mode of operation/time−pressure correlation
slow bulk liquid-phase reaction	$Ha \leq 0.2$, $(AL - 1)Ha^2 \ll 1$	gas- and liquid-phase filled batchwise
		$$\ln\left(\frac{P_B(t)}{P_B(t=0)}\right) = -m_B \frac{1}{\frac{1}{k_L a} + \frac{1}{k_{1,app}}} \frac{V_L}{V_G} t$$
fast pseudo-first-order regime	$2 \leq Ha \ll E_{B,\infty}$	liquid phase in batch, gas phase:
		batchwise $\quad \ln\left(\frac{P_B(t)}{P_B(t=0)}\right) = -m_B \sqrt{k_{1,app} D_B} \frac{S}{V_G} t$
		semibatch $\quad \frac{V_{sv}}{RT_{sv}} \frac{dP_{B,sv}}{dt} = -m_B \sqrt{k_{1,app} D_B} \frac{P_{r,B}}{RT} St$

[a] $Ha_B = \sqrt{k_{1,app} D_B / k_{L,B}} > 1$ (Hatta number). $AL = V_{bulk}/V_{film}$ (Hinterland ratio).
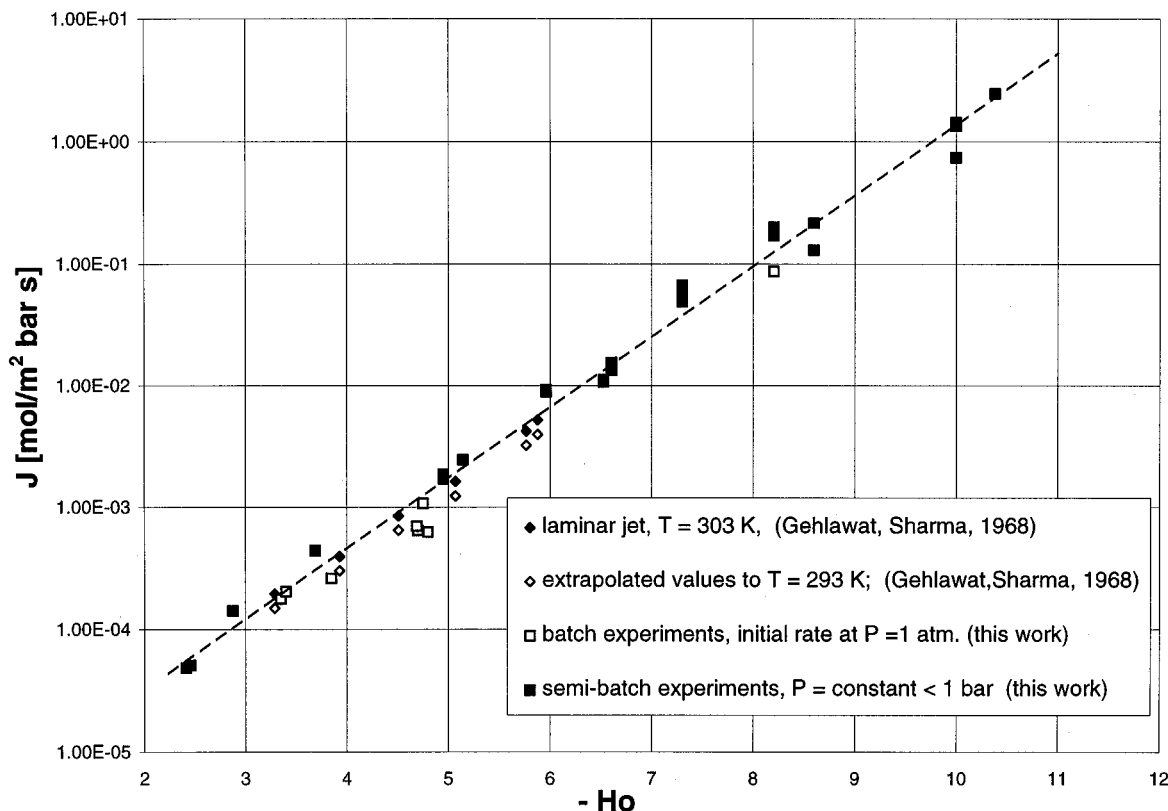
Figure 6. Comparison of absorption flux data for isobutene in sulfuric acid solutions at 293−303 K.

6.3. Analyzing the Absorption Experiments.

From the modeling study it is now clear that the conditions for operation in the fast pseudo-first-order absorption regime are more stringent than was previously expected. For the full-batch experiments the equations in Table 2 can be used to obtain an indication of the upper partial pressure of the butene used for which this equation holds. Indications for these pressures are given in Table 4 for *trans*-2-butene. For isobutene it was not possible to conduct reliable full-batch experiments for acid concentrations exceeding 86 wt %. For full-batch experiments at 76 and 86 wt % the upper partial pressures for the pseudo-first-order regime, experimentally determined at approximately 115 and 10 mbar, were reasonably estimated as 110 and 4 mbar, respectively, by using $D_B\Gamma_B = 10D_A$ and the criterion $Ha_B < 0.01E_{B,\infty}$. For the absorption experiments using the 64 wt % acid solution, the experimentally determined upper limit (250 mbar) was more stringent than the one calculated ($\approx$1000 mbar). The

isobutene solubility at this acid concentration might be somewhat underestimated.

For *trans*-2-butene it is found that the experimentally determined upper operating pressures for kinetic experiments using 71, 79, and 86 wt % acid solutions (150, 90, and 65 mbar; see Table 4) are significantly lower than the ones determined by the estimation method mentioned ($\gg$1000, $\gg$1000, and 700 mbar, respectively). At 90 and 96 wt % acid concentrations these upper partial pressures are reasonably predicted, 74 and 4 mbar, when compared to the experimentally found values of 35 and 15 mbar. Probably the solubility of the butene is somewhat underestimated in the intermediate regime 50−85 wt % and somewhat overestimated in the high acid regime (>90 wt %).

Using the kinetic rate constant correlation equations (9) and (10) for isobutene and *trans*-2-butene, respectively, the values of $Ha_B/E_{B,\infty}$ at bulk phase conditions can be estimated. In Table 5 this criterion is evaluated for the experimental conditions, using a conservative

Table 3. Absorption Fluxes for Isobutene in Sulfuric Acid Solutions at 293.1 K

wt % H_2SO_4	reaction regime	P_B [10^{-2} Pa]	$m\sqrt{k_{1,app}D}$ [m/s][a]	m[b]	D[b] [10^9 m^2/s]	$k_{1,app}$[c] [1/s]
40.5	fast pseudo-first-order	500	1.16×10^{-6}	0.056	0.49	9.10×10^{-1}
45.2	fast pseudo-first-order	400	3.42×10^{-6}	0.053	0.45	3.00×10^{0}
48.9	fast pseudo-first-order	1000	4.25×10^{-6}	0.055	0.41	1.53×10^{1}
54.0	fast pseudo-first-order	1000	6.26×10^{-6}	0.051	0.37	4.10×10^{1}
56.5	fast pseudo-first-order	140	1.06×10^{-5}	0.051	0.35	1.30×10^{2}
61.9	fast pseudo-first-order	1000	1.68×10^{-5}	0.051	0.30	3.66×10^{2}
62.5	fast pseudo-first-order	1000	2.59×10^{-5}	0.051	0.30	8.81×10^{2}
64.1	fast pseudo-first-order	90	4.40×10^{-5}	0.048	0.28	2.93×10^{3}
67.1	fast pseudo-first-order	90	5.91×10^{-5}	0.049	0.27	5.46×10^{3}
71.6	fast pseudo-first-order	14	2.18×10^{-4}	0.055	0.21	7.37×10^{4}
75.5	fast pseudo-first-order	70	2.64×10^{-4}	0.063	0.18	9.70×10^{4}
76.0	fast pseudo-first-order	30	3.25×10^{-4}	0.064	0.18	1.70×10^{5}
80.2	fast pseudo-first-order	40	1.66×10^{-3}	0.081	0.15	2.00×10^{6}
86.0	fast pseudo-first-order	18	4.5×10^{-3}	0.13	0.10	1.50×10^{7}
88.3	fast pseudo-first-order?	20	7.7×10^{-3}	0.16	0.10	2.30×10^{7}
96.0	fast pseudo-first-order?	4−32	3.5×10^{-2}	0.59	0.10	3.50×10^{7}
98	fast pseudo-first-order?	10	6×10^{-2}	0.98	0.10	3.60×10^{7}

[a] Reported fluxes are taken from semibatch experiments at given partial pressures, except for the experiments at "1000 mbar", where initial absorption fluxes are taken from batch experiments. Reported flux: the specific molar absorption rate in [mol/m^2·s] at 1 mol/m^3 gas-phase concentration. [b] Estimated using an isobutene−isobutane analogy (Brilman (1998)). [c] Assuming that the conditions for the fast pseudo first order reaction regime are fulfilled.
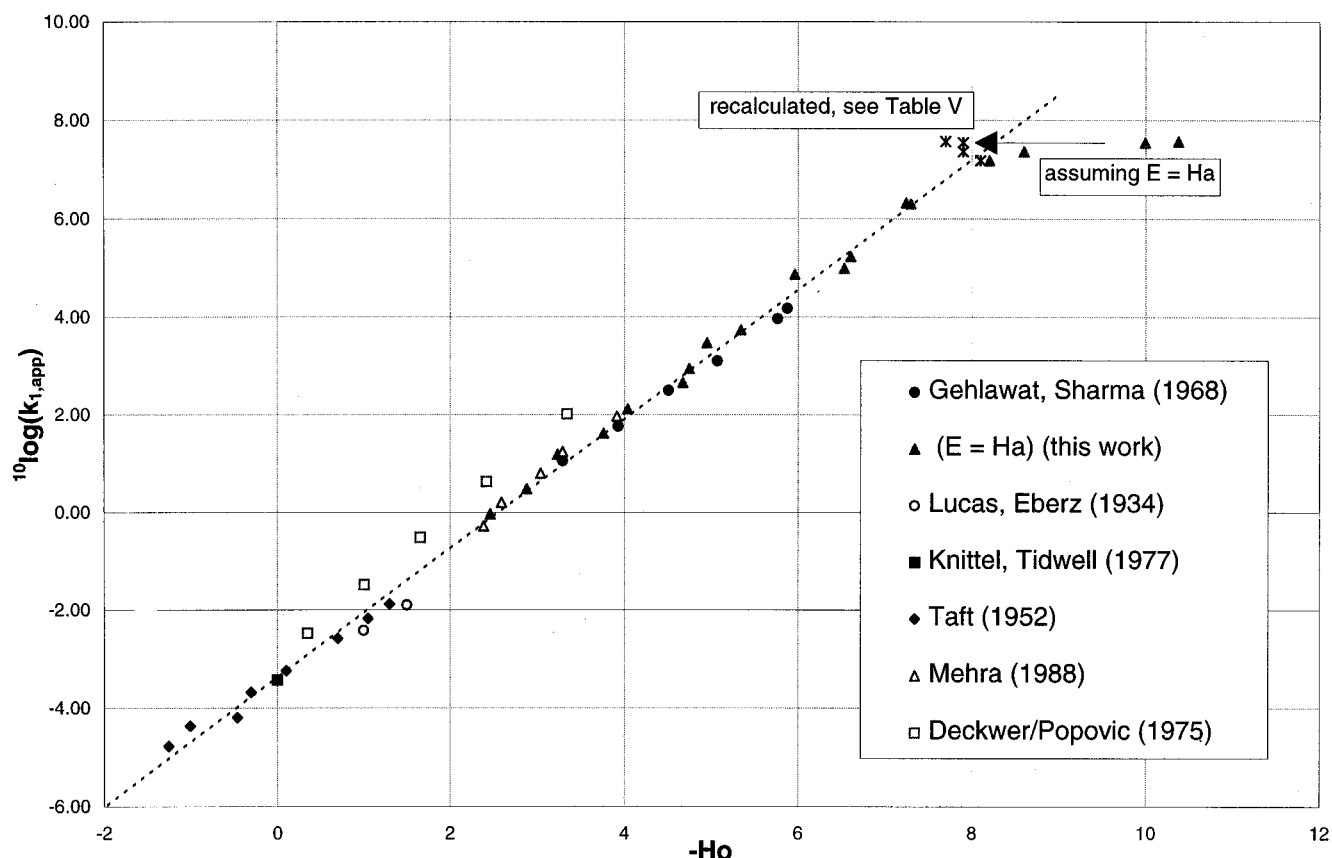
Figure 7. Correlation of kinetic rate constants for the protonation of isobutene in sulfuric acid solutions at 293 K.

estimation for the diffusion coefficient of the acid component, $D_A = D_B$. From the full-batch experiments for *trans*-2-butene absorption in 96 wt % sulfuric acid solution and for isobutene in 86 wt % sulfuric acid solution, it is likely that $D_A \gg D_B$.

Using the estimated $Ha_B/E_{B,\infty}$ values and the generalized curve for this reaction system (Figure 4b), a value for the ratio $(E_B - 1)/(E_{B,\infty} - 1)$ can be found. Using the van Krevelen−Hoftijzer approach (Westerterp et al. (1984))

$$\frac{(c_A)_i}{(c_A)_{bulk}} = \frac{E_{B,\infty} - E_B}{E_{B,\infty} - 1} \qquad (11)$$

the acid concentration at the gas−liquid interface, $(c_A)_i$, can now be estimated. In Table 5 this is done for isobutene absorption experiments at high acid concentrations. Using these acid concentrations, the "interface acidity" $(-Ho)_i$ can be calculated. In Figure 7 the calculated rate constants for these acid concentrations are now plotted at their interface acidity (which is the apparent acidity in the reaction zone for the butene component). These points are indicated with an asterisk.

7. Conclusions

For isobutene and *trans*-2-butene the protonation kinetics for sulfuric acid solutions up to 98 wt % were

Table 4. Absorption Fluxes for *trans*-2-Butene in Sulfuric Acid Solutions at 293.1 K

wt % H_2SO_4	reaction regime[a]	P_B [10^2 Pa]	$m\sqrt{k_{1,app}D}$ [m/s][b]	m^c	D^c [10^9 m²/s]	$k_{1,app}$ [1/s]
30.0	slow reaction			0.070		5.43×10^{-7}
45.0	slow reaction			0.057		2.17×10^{-5}
50.0	slow reaction			0.055		5.89×10^{-5}
54.0	slow reaction			0.054		4.18×10^{-4}
61.4	slow reaction			0.053		2.22×10^{-2}
71.4	fast pseudo-first-order	<150	9.72×10^{-7}	*0.054*	*0.22*	1.50
78.9	fast pseudo-first-order	<90	7.52×10^{-6}	*0.066*	*0.16*	8.12×10^1
86.0	fast pseudo-first-order	<65	8.67×10^{-5}	*0.11*	*0.1*	6.46×10^3
90.0	fast pseudo-first-order	<30	4.00×10^{-4}	*0.18*	*0.1*	4.90×10^4
96.0	fast pseudo-first-order	<10	2.71×10^{-3}	*0.56*	*0.1*	2.51×10^5

[a] Absorption experiments performed in a stirred-cell contactor with flat interface (fast pseudo-first-order regime) and an intensely stirred tank reactor (slow reaction regime). [b] R is the specific molar absorption rate in [mol/m²·s] at 1 mol/m³ gas-phase concentration. [c] Values in italics are obtained by estimation using a 2-butene−isobutane analogy.
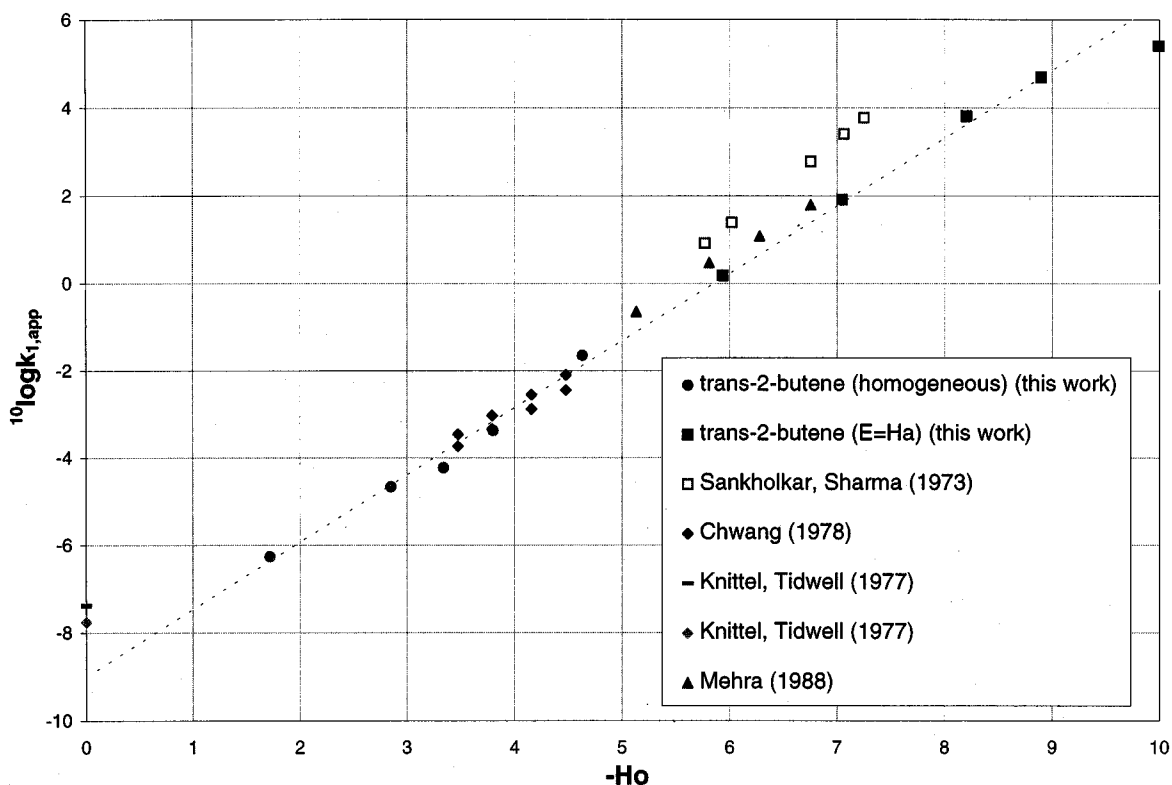
Figure 8. Correlation of kinetic rate constants for the protonation of *trans*-2-butene in sulfuric acid solutions at 293 K.

Table 5. Analysis of Absorption Experiments for *trans*-2-Butene and Isobutene Absorption in Sulfuric Acid Solutions of Different Strength

butene	wt % H_2SO_4	Ha_B	P_{exp} [bar]	$Ha_B/E_{\infty,B}{}^c$	$(c_A)_i/(c_A)_{bulk}$	$(-Ho)_i$
trans-2-butene	71.4	2.2	<150[a]	6.0×10^{-5}		
	78.9	17	<90[a]	3.9×10^{-4}		
	86.0	1.6×10^2	<65[a]	4.4×10^{-3}		
	90.0	6.3×10^2	<30[a]	1.2×10^{-2}		
	96.0	3.7×10^3	<15[a]	9.8×10^{-2}		
isobutene	64.1	1.2×10^2	90[b]	2.3×10^{-3}		
	71.6	4.0×10^2	14[b]	1.7×10^{-3}		
	76.0	1.7×10^3	30[b]	1.1×10^{-2}	1.0	
	80.2	4.8×10^3	40[b]	5.0×10^{-2}	1.0	
	86.0	2.8×10^4	18[b]	1.9×10^{-1}	0.98	8.1
	88.3	5.5×10^4	20[b]	6.0×10^{-1}	0.94	7.9
	96.0	4.6×10^5	4[b]	1.0×10^1	0.86	7.9
	98	6.4×10^5	10[b]	2.4×10^1	0.82	7.7

[a] Upper partial pressure of B in the stirred cell for the kinetic regime. [b] Partial pressure of B in the semibatch experiments used. [c] $E_{B,\infty}$ is calculated according to eq 7, assuming $D_A = D_B$. This is the maximum $Ha_B/E_{B,\infty}$ value for the full-batch experiments (*trans*-2-butene).

studied. Linear correlations of the apparent first-order rate constant with Hammett acidity function *Ho* were found to be valid up to 90 wt % sulfuric acid solutions. This result supports the idea that reaction kinetics for this type of reaction should be based on the activities of the reacting species.

In modeling the reactive absorption processes, an activity-based reaction rate expression was used. It is

not possible to carry out experiments in the instantaneous reaction regime. Moreover, in the simulations, even for Hatta numbers which exceed the theoretical infinite enhancement factor from the penetration model by a factor of 10^6, this was not accomplished.

It should be noted that the criteria usually used for the pseudo-first-order reaction regime are not satisfactory to ensure kinetic measurements (see also Versteeg et al. (1989)), since it was shown that the application of the activity-based reaction rate equation resulted in a more stringent criterion for the kinetic absorption experiments, $Ha_B < 0.01E_{B,\infty}$, which implies a smaller operating window.

Using a relatively simple activity model, the experimentally determined mass-transfer enhancement factors could be reasonably predicted by the absorption model developed from kinetic experiments conducted under well-known reactions conditions, i.e., experiments in the homogeneous reaction regime or the fast pseudo-first-order reaction regime.

Acknowledgment

Notation

a_i = activity of component i [mol/L]

AL = Hinterland ratio

c_i = concentration of component i [mol/L]

D_i = diffusion coefficient component i [m^2/s]

$D_{i,0}$ = diffusion coefficient component i at infinite dilution [m^2/s]

E_B = enhancement factor for gas−liquid mass transfer of component B

$E_{B,\infty}$ = infinite enhancement factor for component B, defined in eq 7

Ha_B = Hatta number for component B

He_B = Henry's law constant for component B [mol/m^3·Pa]

Ho = Hammett acidity function ($Ho = -\log(a_{H^+})$)

$K_{eq,c}$ = concentration-based equilibrium constant, $=c_C/c_A c_B$ [L/mol]

$k_{1,app}$ = apparent first-order reaction rate constant, defined in eq 1 [1/s]

k_G = gas-phase mass-transfer coefficient [m/s]

k_h^* = reaction rate constant, $=k_T\gamma_B$ [L/mol·s]

k_L = liquid-side mass-transfer coefficient [m/s]

$k_L a$ = volumetric, liquid-side mass-transfer coefficient [1/s]

k_T = reaction rate constant [1/s]

$k^\#$ = reaction rate constant, $=k_T\gamma_B\gamma_A$ [L/mol·s]

m_B = distribution coefficient for gas-phase component B, $m_B = (c_{B,L}/c_{B,G})^i$

P_B = partial pressure component B [Pa]

R = molar gas constant (=8.314) [J/mol·K]

R_i = volumetric reaction rate for component i [mol/m^3·s]

S = geometric surface area of the stirred-cell apparatus [m^2]

t = time [s]

T = temperature [K]

V = volume [m^3]

x = place coordinate [m]

Greek Symbols

γ_i = (concentration-based) activity coefficient of component i

Γ_i = thermodynamic correction factor for the diffusion equation

η = viscosity [kg/ms]

Sub- and Superscripts

A = reactant originating from liquid phase (acid)

B = reactant originating from the gas phase (butene)

bulk = liquid bulk phase conditions

film = mass-transfer zone at the gas−liquid interface

G = gas phase

H$^+$ = proton

i = at the gas−liquid interface

L = liquid phase

r = reactor conditions

sv = conditions in the gas-phase storage vessel (for gas in semibatch experiments)

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