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Absorption Methods for the Determination of Mass Transfer Parameters of Packing Internals: A Literature Review

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Methods for the determination of mass-transfer coefficients and effective interfacial areas in packed absorption columns are reviewed. For each parameter, the methods are grouped into categories on the basis of their physical principle; the chemical systems used, experimental protocol, and the advantages and inconveniences are discussed. The treatment of end effects, the influence of packed bed height, and the recent efforts in standardization of measurement methods are also treated. The aim of the review is to give a broad overview of the methods used in literature in the last eight deca-des, some of which might be reconsidered in the light of modern measurement techniques and to evaluate them in relation to precision, practicality and hazardousness thereby to facilitate the search for reliable, precise, and convenient experimental practices.

Keywords: mass-transfer coefficient, interfacial area, absorption, desorption, packed column

Introduction

In counter-current separation processes, such as distillation, extraction, and gas absorption, the separation is based on the transfer of one or more components between the fluid phases in contact. To improve the efficiency of these processes by the increase of mass transfer between the phases, the contact between the phases is intensified by the application of phase contactor devices: trays (plates) or packings. The contact of the phases is stagewise in the case of trays, and continuous with packings. The use of packed columns is especially widespread in absorption owing to their advantages over tray columns. Packings offer lower pressure drop, higher capacity, and higher interfacial area. Random packings have been used since the beginning of the 20th century. They consist of discrete structural elements that are randomly dumped in a column to make the absorption section. Typical sizes range from 1 to 10 cm. Structured packings are made up of corrugated metal sheets or wire mesh that are placed vertically into the column as blocks of assembled layers. The corrugation sizes are typically between 0.5 and 2 cm with block sizes on the order of 25 cm. Structured packings are less commonly used in absorption.¹ They tend to be better suited for low pressure

applications as they offer particularly low pressure drop and increased capacity and efficiency, but at a higher cost.

For the design and analysis of separation columns reliable mass transfer parameters are needed, especially with the increased use of rate-based models for process simulations. Mass-transfer coefficients relate the mass transfer flux to the driving force which is the mass concentration potential difference inducing it. Depending on the choice of concentration difference, multiple mass-transfer coefficients can be defined. If the concentrations in the bulk phases are used, we speak of overall mass-transfer coefficients:

$$\varphi = K_G(y - y^*) = K_L(x^* - x) \quad (1)$$

where φ is the rate of absorption per unit surface ($\text{mol}/[\text{m}^2 \text{ s}]$), K_G is the gas-side, K_L is the liquid-side overall mass-transfer coefficient ($\text{mol}/[\text{m}^2 \text{ s}]$), y is the mole fraction of the solute in the gas phase, and x is the mole fraction in the liquid phase. The superscript * denotes an equilibrium concentration: for example, y^* is the gas phase solute concentration at equilibrium with the liquid bulk solute concentration x . Note that K_G and K_L have the same physical meaning; they are just written from the perspective of the gas or of the liquid phases.

The mass-transfer coefficients of the individual phases (k_G for gas and k_L for liquid) characterize the mass transfer conductance of their respective phases and therefore have different physical meanings. In this case, the driving force is written as the difference between the bulk and interfacial concentration:

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$$\varphi = k_G(y - y_i) = k_L(x_i - x) \quad (2)$$

where index i refers to the interface. The overall resistance to mass transfer between the two phases is the sum of the resistances of the individual phases. The overall gas-side mass-transfer coefficient K_G is then expressed as:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L} \quad (3)$$

where m gives the equilibrium relation between gas- and liquid-side concentrations:

$$y = mx \quad (4)$$

If a chemical reaction is consuming the solute in the liquid phase then the absorption flux will be accelerated and the effective liquid-side mass-transfer coefficient is then expressed as $k_{L,R}$, the value of which is greater than k_L .

The individual determination of each film coefficient would require measurements of interfacial and bulk concentrations of the solute. However, current experimental techniques are not capable of interfacial measurements. The individual film coefficients can thus only be determined under conditions where the resistivity of one of the phases is neglected. Various reactive absorption methods have been used to approach such conditions but the only case when there is absolutely no resistivity in one of the phases is when this phase is purely the solute because there is then no concentration gradient. In every other situation, neglecting the resistivity is an approximation, the validity of which has to be verified.

The total absorption rate per unit volume of packing depends directly on the exchange area available that is characterized by the effective interfacial area mass transfer parameter a_e (m^2/m^3):

$$\Phi = a_e \varphi = k_G a_e (y - y_i) = k_L a_e (x_i - x) \quad (5)$$

Experimental measurements of concentrations changes in one of the phases yields Φ from which $k_G a_e$ and $k_L a_e$ can then be derived. The values of k_G and k_L are then obtained by dividing by a_e obtained from separate measurements. Errors in a_e will propagate into the mass-transfer coefficients. To avoid excessive uncertainties, it is therefore best to use mass transfer parameters obtained all in the same facility. In particular, when sizing a column with k_G or k_L correlations, the latter should be used only with the effective area correlation from which they were derived in order to be coherent with experimentally measured absorption rates.

The mass transfer performance of a packed column can be expressed either on the basis of transfer units or theoretical plates. The change in composition of one of the phases is given by:

$$\int_{y_{\text{out}}}^{y_{\text{in}}} \frac{1}{y - y^*} dy = \frac{HK_G a_e}{G} \quad (6)$$

where G , the column gas molar flow rate per sectional area ($\text{mol}/[\text{m}^2 \cdot \text{s}]$), is assumed constant and a_e is the effective interfacial area (m^2/m^3). If the equilibrium concentration y^* is constant between inlet and outlet then this equation describes an exponential decay law towards equilibrium. One transfer unit is then defined to represent a fractional progress of 63% or $1 - e^{-1}$ toward this equilibrium condition in the phase considered. This happens when the integrated term is equal to unity, which leads to the definition of the height of one transfer unit:

$$\text{HTU}_{\text{OG}} = \frac{G}{K_G a_e} \quad (7)$$

The number of transfer units of a column where the integral is not unity is then defined as:

$$\text{NTU}_{\text{OG}} = \frac{H}{\text{HTU}_{\text{OG}}} = \frac{HK_G a_e}{G} \quad (8)$$

Analogous equations can be derived for the liquid phase, as well:

$$\int_{x_{\text{out}}}^{x_{\text{in}}} \frac{1}{y - y^*} dx = \frac{HK_L a_e}{L} \quad (9)$$

$$\text{HTU}_{\text{OL}} = \frac{L}{K_L a_e} \quad (10)$$

$$\text{NTU}_{\text{OL}} = \frac{H}{\text{HTU}_{\text{OL}}} = \frac{HK_L a_e}{L} \quad (11)$$

where L is the molar flux of the liquid ($\text{mol}/[\text{m}^2 \cdot \text{s}]$). NTU_{OG} and NTU_{OL} have different numerical values, but both can be applied, as long as the appropriate HTU value is used. Depending on the composition difference, and thus on the mass-transfer coefficient used, NTU and HTU can be of overall nature (gas- or liquid-side) or defined for one of the phases only. They are determined experimentally by measuring concentration changes in one of the phases between the inlet and outlet of the column. They characterize volumetric mass-transfer coefficients $k_G a_e$ or $k_L a_e$.

While transfer units are preferred in absorption, the concept of height equivalent to a theoretical plate (HETP) is applied widely in distillation design. The height of packed bed is then expressed as the product of the number of theoretical plates and the HETP. Both HETP and HTU measure the performance of the packing, although HTU-NTU method is physically more fundamental.

Ever since the introduction of the two-film theory of interfacial mass transfer in the 1920s, a vast number of studies has been performed for the determination of the mass transfer parameters $k_G a_e$, $k_L a_e$ and a_e of different random and structured packings, using a variety of methods. Based on measurement results, a large number of empirical and semi-empirical (based on theoretical considerations) correlations have been proposed for these mass transfer parameters expressed in terms of operating conditions, packing geometry, and physical properties of the gas and liquid phases. An extensive review of these correlations has been given by Wang et al.² Considering just the last 20 years, Figure 1 illustrates that even recent correlations lead to considerably different calculated mass transfer parameter values. These disparities reflect those of experimental results obtained in the various apparatus, and illustrate the need for a cautious evaluation of experimental methods. Part of the differences may result from using the correlations beyond their range of validity whether they are hydraulic or fluid physical property parameters. The latter situation can easily arise despite the inclusion of viscosity, density, or surface tension terms in the correlations, simply because the underlying experiments have usually been performed within only a small range of values, if any, of such properties. Extrapolation to other packings can be more successful (especially for structured packings) when terms related to the packing geometry are taken into account.

The above discussion shows the need for improving the precision and accuracy of experimental methods in order to

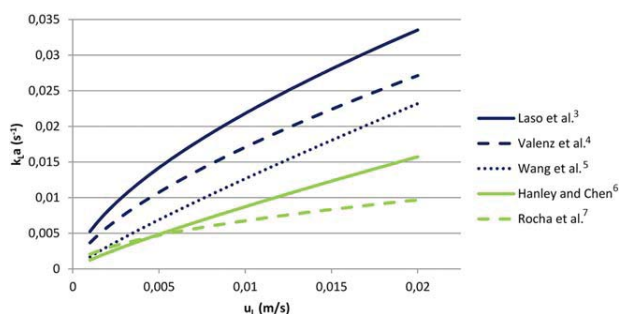


Figure 1. An example for the deviation of correlations: predicted $k_L a$ values for Mellapak 250.Y (based on Wang et al.⁵).

The $k_L a$ values are adjusted to the toluene-water system of Wang et al.⁵ by assuming square-root dependency to liquid side diffusivity of the solute. [Color figure can be viewed at wileyonlinelibrary.com]

derive reliable and coherent sets of data. Errors can originate from a number of sources such as hydrodynamic uncertainties, by neglecting or underestimating end-effects, and phase maldistributions, chemical uncertainties, leading to ill assessment of the absorption regime, or yet underestimating the contribution of one of the phases to the mass transfer resistance, etc.⁸ In light of these difficulties, several authors insisted in recent years on the standardization of the methods.^{8–10}

The aim of the present work is to give a comprehensive overview of the experimental methods that have been used to determine the mass transfer parameters k_G , k_L , and a_e , from the earliest experiments in the 1920s to the most recent investigations. This work brings up to date previous more specific reviews on the determination of a_e ,¹¹ or on the different chemical methods for the determination of all three parameters^{12,13} along with a review of broader scope¹⁴ and complements recent articles^{8,9} that cover only partial lists of the possible methods. We have chosen to make a broad review in order to assess the possibility of reconsidering older methods that may be worthy in light of modern analytical techniques. For every method, references are given along with the packing type and chemical system used. Correlations established based on the experiments are not included, as they are not likely to be directly comparable to each other due to different gas and liquid load and packings applied. Some of these correlations can be found in the review of Wang et al.² It would be also interesting to collect experimental data obtained under the same conditions by different authors and compare them also with predicted data, however, this is outside the scope of the present work, and could be the subject of a future paper. We must also note that although this article focuses on packings, the methods reviewed could equally be applied to the determination of mass transfer parameters of other types of column internals, such as trays or spray nozzles.

Methods for each of the mass transfer parameters k_G , k_L , and a_e are presented and discussed separately, categorizing the measurement techniques by physical or chemical principle. Different procedures to estimate end-effects, packed bed height effects on the mass transfer parameters are also reviewed and discussed as they are an integral part of the source of data disparity among authors. Last, we review the literature proposals for standardization of the measurement methods.

Determination of the Effective Interfacial Area

Knowledge of the effective interfacial area for mass transfer is crucial, especially since errors in its evaluation will propagate into the determination of k_G and k_L that are calculated by dividing the volumetric mass-transfer coefficients by the interfacial area, for example:

$$k_G = \frac{k_G a_e}{a_e} \quad (12)$$

Moreover, according to Ahmadi¹⁵ and Maćkowiak and Maćkowiak,¹⁶ the results of rate-based models for column and process design are particularly sensitive to the value of a_e .

In the literature dealing with column packings, different methods have been developed to determine the area, however, they do not always measure the same type of area. The methods can be classified into the following groups based on the physical or chemical measurement principle:

- chemical absorption,
- vaporization of a pure liquid,
- physical absorption,
- tomography,
- colorimetry,
- sublimation of the packing.

The value and significance of the determined area varies according to the type of method used. Some measure the interfacial area, others a wetted area and others yet an effective area all of which can have different values. It is very important to clearly state what type of area is measured for its appropriate use in subsequent calculations. For example, a correlation for “ a ” obtained by evaporation would not be appropriate for use in a physical absorption process calculation due to saturation of stagnant zones that would reduce the effective area for mass transfer of a solute but not for evaporation. This is one of the reasons why film mass-transfer coefficient correlations should be used with the corresponding area correlation from which they were derived, and not mixed between different authors.

In the following sections, we first review the definitions and significance of the various types of areas encountered in packings. Then the different types of methods will be discussed, highlighting also the nature of the interfacial area measured.

Specific areas defined in packings

In the literature dealing with column packings, several types of specific areas are defined. To illustrate these areas, Figure 2 schematizes a liquid flow around a single packing element such as a Raschig ring.

The geometric area of the packing elements per unit volume of column, a_g , can be calculated from the dimensions of the packing. It is a fixed quantity for structured packings, but in the case of random packings, it depends on the filling density, or the number of packing elements per m^3 .

The wetted area a_w is defined as the portion of the geometric area covered with liquid. By definition, it cannot be larger than the latter. The value of the wetted area is influenced by the gas and liquid flow distribution patterns and the wettability of the packing. The latter is determined by the surface tension of the liquid and the packing material. Plastic packings have lower wettability than metal and ceramic ones. Porosity and surface roughness increase wettability.

The interfacial area, a_i , is defined as the total contact surface between the gas and liquid phases. This area is not clearly distinguished from a_w in the literature; the majority of the articles

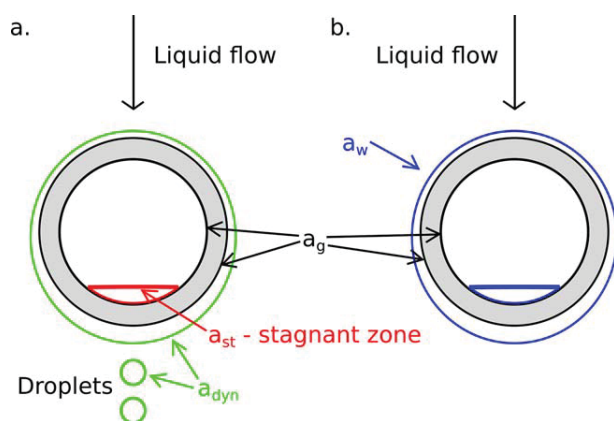


Figure 2. Different surface areas identified schematically for liquid flowing around a single Raschig ring: (a) static and dynamic areas, (b) wetted area.

[Color figure can be viewed at wileyonlinelibrary.com]

claiming to determine a_w implicitly assume that liquid is only present on the surface of packings. However, liquid between packing elements in the form of droplets and rivulets, and liquid on the column wall contribute to mass transfer, meaning that a_i is always higher than a_w . The ratio between the two areas is greater for random than for structured packings.¹⁷ Puranik and Vogelpohl¹⁸ discriminate between a static (a_{st}) and a dynamic (a_{dyn}) part of the interfacial area (although they considered it to be equal to a_w), assuming that they are the interfacial area belonging to static and dynamic liquid hold-up, respectively:

$$a_i = a_{st} + a_{dyn} \quad (13)$$

The static part of interfacial area is not renewed, thus it is affected by saturation or depletion of the solute or of chemicals, and after some time no longer participates in the mass flux. Its ratio to the total interfacial area is likely to be higher for early random packings such as Raschig rings, and lower for structured and modern random packings, which have more open forms, as one of the main goals of the development of new packings is the elimination of stagnant liquid pools. The dynamic part of the wetted area is continuously renewed by the liquid flow, and thus remains active for mass transfer of the solute.

Last and most important is the effective interfacial area, a_e , which is the part of the interfacial area, where mass transfer actually takes place. Its value can be very different from the geometric and/or wetted areas. It is always lower than the interfacial area, since a fraction of a_i may be inactive due to stagnation and local saturation or depletion of a species in the liquid bulk. In addition, liquid can flow along the column wall as well as between packing elements (droplets, rivulets) and thereby increase the effective area relative to the geometric area, more so with random packings than with structured ones.¹⁷ Kolev et al.¹⁹ have reported instances where a_e is twice the value of a_g .

The magnitude of the effective interfacial area depends on the nature of the mass transfer process taking place in the column. With evaporation of a pure liquid, the entire interfacial area is active since there is no concentration change in the liquid phase. With physical absorption, a_e is lower than a_i and

equal to a_{dyn} . The stagnant liquid parts, that is, the zones without a sufficiently high liquid flow rate and/or turbulence to ensure renewal of the phase, become saturated with the solute, so they become inactive. In the case of desorption, the same situation occurs due to depletion of the solute. Shulman^{20,21} related the ratio of a_e and a_{dyn} to that of total and dynamic liquid hold-up. With chemical absorption, the reaction rate and the change of solvent capacity have important effects. This is described by Joosten and Danckwerts²² with a parameter γ_{JD} defined as:

$$\gamma_{JD} = \frac{C}{E} \quad (14)$$

where C is the factor by which the reaction increases the absorption capacity per liquid unit volume, E is the enhancement factor, that is, the ratio of the absorption rates with and without reaction. In the case of a slower reaction with high absorbent capacity (e.g., buffer solutions), $\gamma_{JD} \gg 1$, the liquid does not become saturated and the entire liquid surface will be active for mass transfer. However, if $\gamma_{JD} = 1$, such as with an instantaneous reaction, then although a greater quantity of the solute can be absorbed in the liquid than without reaction, the rate of absorption increases proportionally to the capacity, such that the time to saturate the stagnant liquid zones is unchanged. This means that saturation will reduce the effective area, which will be equal to the one in the case physical absorption.

Puranik and Vogelpohl¹⁸ proposed correlations for a_{st} and a_e of random packings based on available literature data. Their correlations apply to various mass transfer situations, and can be used to illustrate the differences of a_e under different situations. Figure 3 shows the values calculated as a function of liquid load within the range of validity for a packing with $a_g = 300 \text{ m}^2/\text{m}^3$, using water as liquid. The static area in the correlation depends only on the properties of the liquid and a_g , giving a constant a_e/a_g in our calculation. The effective interfacial area is shown for different absorption situations with different values of the Hatta number (Ha) with the latter varying only from an increase in the liquid phase reagent concentration. In this case, C increases faster with the reagent concentration than E . Physical absorption corresponds to the situation where Ha is zero, and $a_e = a_{dyn}$. The case of $Ha = 1$ corresponds to an intermediate reaction speed. As Ha increases, an increasing part of a_{st} becomes effective for the mass transfer, and thus the effective area increases: $a_e = \eta(Ha) \cdot a_{st} + a_{dyn}$. The case with $Ha = \infty$ corresponds to an infinitely fast reaction, the limiting case where the entire interfacial area is effective that is $a_e = a_{st} + a_{dyn}$. Thus the difference between the solid grey line ($Ha = 0$) and the dashed black line ($Ha = \infty$) is simply a_{st} . According to these correlations, a_{st} is significant, and of the same order of magnitude as a_e and actually higher than a_e at low liquid flow rates and Ha . These results illustrate the importance of assessing the type of area that is measured or applicable for a given measurement method.

In summary, several types of area can be defined and measured in packed columns. The values of these area may be significantly different, so it is important to be aware of the type of area that is obtained and to be cautious to use the appropriate one for a given absorption situation. For example, a_i can be used to determine k_G from $k_G a$ measured by vaporization, but a_{dyn} should be used for physical absorption and a_e for chemical absorption.

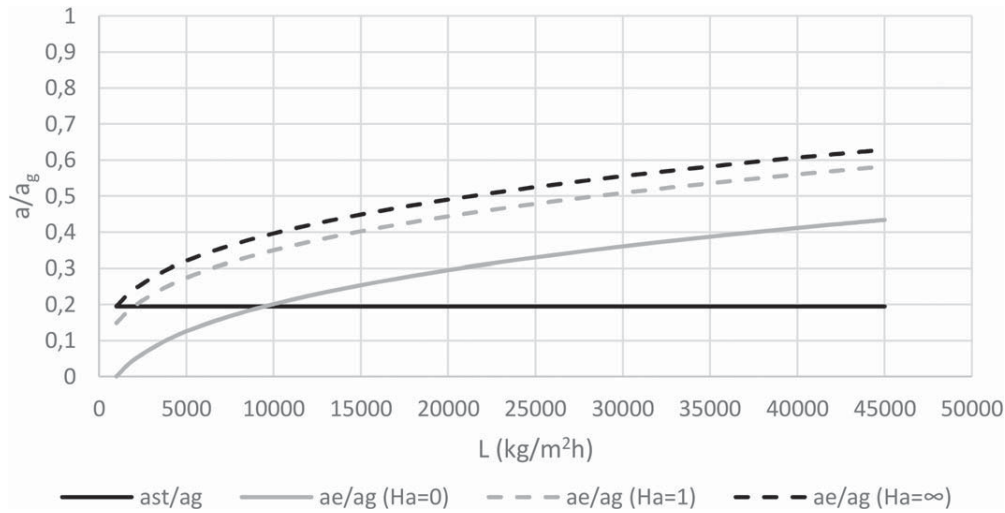


Figure 3. Static and effective interfacial area calculated by the correlations of Puranik and Vogelpohl¹⁸ for a random packing with $a_g = 300 \text{ m}^2/\text{m}^3$, with water as liquid phase.

Chemical absorption

The most popular method for determining a_e is chemical absorption with a reaction system in either the fast or intermediate reaction regimes. Overviews of this group of methods are given by Sharma and Danckwerts¹² and Laurent et al.¹³ as applied to simple systems with analytical solutions. Last and Stichlmair²³ propose a method using fast second-order reactions, but to our knowledge, it has not yet been applied experimentally. In some of the more recent works,^{24,25} complete column models have been developed, which are used to determine the interfacial area by using the latter as regression parameter to match measured mass transfer fluxes. In this section, we will describe these various methods and the chemical systems with which they have been applied.

Prior to discussing the methods, it is important to define two dimensionless numbers: the enhancement factor (E) and the Hatta number (Ha). The enhancement factor expresses the extent with which the chemical reaction increases the rate of absorption compared to physical absorption:

$$E = \frac{k_{L,R}}{k_L} \quad (15)$$

where $k_{L,R}$ is the mass-transfer coefficient with chemical reaction. The Hatta number is the ratio of the rate of reaction to the rate of diffusion in the liquid film. As Ha increases, E converges to the enhancement factor of infinitely fast reaction E_{inf} . In this hypothetical case, the reaction takes place exclusively on the interface. For a detailed treatment of absorption in the presence of reactions, the reader is referred to the book of Danckwerts.²⁶ A classification of reaction regimes and corresponding expressions relating E and Ha can also be found in Last and Stichlmair.²³

Fast Reactions. Literature studies using fast chemical absorption systems for the determination of a_e are listed in Table 1. They apply the methodology and chemical systems that are described hereafter.

Methodology. In order to determine a_e by chemical reaction, we need to know the reaction kinetics and the system must satisfy several constraints:

- negligible gas side resistance,

- $Ha \ll E_{\text{inf}}$,^{28,58}
- $Ha > 3$.^{12,29}

The first constraint ensures that the concentration of solute at the interface is the same as in the bulk gas. The second constraint ensures that the reaction system is of pseudo- m th order relative to the solute, which simplifies the analysis, as the concentration of the liquid phase reagent is constant in the film, and the third sensitizes the measured rate of absorption to a_e by effectively removing any dependence to (physical) liquid-side mass-transfer coefficient.

More precise forms of the second constraint are given by Henriques de Brito et al.⁴¹ as:

$$Ha < \frac{1}{2} E_{\text{inf}} \quad (16)$$

and by Tsai et al.¹⁷ as:

$$Ha < \frac{1}{5} E_{\text{inf}} \quad (17)$$

Other forms of the third condition can be found in the literature, such as $Ha > 5$,¹³ $Ha > 2$,⁴⁴ $E > 5$,²⁷ or $E > 3$.¹⁹ The reactions fulfilling these constraints are sometimes called moderately fast,¹² to emphasize that they are not very fast or instantaneous reactions.

To illustrate the method of chemical absorption with fast reaction, consider the following irreversible reaction:



where A is the absorbed component, B is the reagent in the liquid phase, ν is the stoichiometric coefficient, and the local rate of reaction is $k[A]^m[B]^n$ with k the rate constant. For the above reaction, E_{inf} can be expressed as^{28,58}:

$$E_{\text{inf}} = 1 + \frac{D_B B^0}{D_A \nu A^*} \quad (19)$$

where B^0 is the bulk concentration of B , A^* is the concentration of A at the surface of the liquid phase, and D_A and D_B (m^2/s) are the diffusivities of A and B in the liquid phase.

The first constraint, negligible gas phase resistance, ensures that A^* is the solubility of A in the liquid phase without reaction as determined by the bulk gas phase concentration of A .

Table 1. Investigations Using Chemical Absorption with a Fast Reaction to Determine a_c

Source	Packing	Gas	Liquid	Order of Reaction
Yoshida and Miura ²⁷	Raschig rings	CO ₂ in air	NaOH (aq) KOH (aq)	Pseudo-first
Widwans and Sharma ²⁸	Raschig rings	CO ₂ in air	NaOH (aq) MEA (aq)	Pseudo-first
Jhaveri and Sharma ²⁹	Raschig rings	Isobutylene O ₂ of air	H ₂ SO ₄ CuCl + CuCl ₂ + HCl (aq) dithionite + NaOH (aq)	Pseudo-first or pseudo-zero
Danckwerts and Rizvi ³⁰	Raschig rings, Pall rings, Intalox saddles	O ₂ of air	Na ₂ SO ₃ + CoSO ₄ (aq)	Second
Onda et al. ³¹	Raschig rings	Pure O ₂ , O ₂ in air, O ₂ of air	Na ₂ SO ₃ + CoSO ₄ (aq)	Pseudo-first and pseudo-second
Sahay and Sharma ³²	Raschig rings, Pall rings, Intalox saddles	O ₂ of air	dithionite (aq)	Pseudo-first and pseudo-second
Linek et al. ^{33,34}	Raschig rings, Pall rings	CO ₂ in air	NaOH (aq) DEA (aq)	Pseudo-first
Alper ³⁵	Raschig rings, Pall rings	Pure O ₂	Na ₂ SO ₃ + CoSO ₄ (aq)	Pseudo-second
Merchuk ³⁶	Fenske helices, porous ceramic cylinders	O ₂ of air	Na ₂ SO ₃ + CoSO ₄ (aq)	Pseudo-second
Rizzuti et al. ³⁷	Raschig rings, flat rings, spi- rals, saddles	CO ₂ in air	NaOH (aq)	Pseudo-first
Neelakantan and Gehlawat ³⁸	Rings	O ₃ in air	Phenol + base (aq)	Pseudo-zero
Linek et al. ³⁹	Raschig rings	Pure O ₂	(NH ₃) ₂ SO ₃ (aq)	Pseudo-first
Weiland et al. ⁴⁰	Pall rings	CO ₂ in air	NaOH (aq)	Pseudo-first
Henriques de Brito et al. ⁴¹	Goodloe, Montz A2	CO ₂ in air	NaOH (aq)	Pseudo-first
Benadda et al. ⁴²	Raschig rings, Mellapak 125.Y, 250.Y, 500.Y	CO ₂ in air	NaOH (aq)	Pseudo-first
Weimer and Schaber ⁴³	Raschig rings	O ₂ (21%)	Na ₂ SO ₃ + CoSO ₄ (aq) CuCl (aq)	Pseudo-first
Nakajima et al. ⁴⁴	Mellapak 250.Y, Hiflow	CO ₂ of air	NaOH (aq) KOH (aq)	Pseudo-first
Duss et al. ^{45,46} ; Duss and Menon ⁴⁷	Raschig rings, Pall rings	CO ₂ in N ₂	NaOH + sugar (aq)	Pseudo-first
Kolev et al. ¹⁹ ; Nakov et al. ⁴⁸	Nutter rings	CO ₂ of air	NaOH (aq)	Pseudo-first
Hoffmann et al. ⁸	Raschig Super-Ring	CO ₂ in air	NaOH (aq)	Pseudo-first
Green ⁴⁹	Pall rings	CO ₂ in air	NaOH (aq)	Pseudo-first
Tsai et al. ^{17,50,51}	Mellapak 250.Y	CO ₂ of air	NaOH (aq)	Pseudo-first
Alix and Raynal ⁵² ; Alix et al. ⁵³	Mellapak 250.X, 250.Y, 250.YS, 500.Y, 2Y, Mella- pak Plus 252.Y Flexipac 1Y, Prototype 500	CO ₂ in air, or of air	NaOH (aq)	Pseudo-first
Aferka et al. ⁵⁴	IMTP50, 4D	CO ₂ of air	NaOH (aq)	Pseudo-first
Valenz et al. ⁴	Mellapak 752.Y	CO ₂ of air	NaOH (aq)	Pseudo-first
Wang et al. ^{55,56}	Mellapak 250.Y, 350.Y, 452.Y, 500.Y	O ₂ of air, or in pure form	Na ₂ SO ₃ + CoSO ₄ (aq)	Pseudo-second
Rejl et al. ⁵⁷	Mellapak 2X, 250.X, 250.Y, Flexipac, Raschig Super- Pak, Raschig Super-Ring, Pall rings, GT-Pak 350Y, 350Z	CO ₂ in air	NaOH (aq)	Pseudo-first
Kunze et al. ¹⁰	Super-Pak 250.Y	CO ₂ in air	NaOH (aq)	Pseudo-first
	Pall rings, Mellapak 250.Y	CO ₂ of air	NaOH (aq)	Pseudo-first

The second constraint ensures that the reaction is of pseudo- m th order by keeping the concentration of B constant through the liquid film (equal to B^0) which rules out very fast reactions and also means that a great excess of B is preferred in the experiments. Component A reacts within a very short distance of the interface, such that its concentration is zero in the bulk of the liquid phase.²⁹ Then the rate of absorption per unit volume (Φ , mol/[m³·s]) can then be written as:

$$\Phi = Ek_L a_c A^* \quad (20)$$

and the Hatta number is then given as¹²:

$$\text{Ha} = \frac{\sqrt{\frac{2}{m+1} D_A k (A^*)^{m-1} (B^0)^n}}{k_L} \quad (21)$$

The third constraint ensures that the reaction is still fast enough so that the rate of physical absorption is negligible

compared to reaction rate, eliminating thereby the dependency of E on k_L . In this reaction regime, where the second and third constraints are valid, the following relation is true for the double-film model:

$$E = \frac{\text{Ha}}{\tanh \text{Ha}} \quad (22)$$

and consequently $E \approx \text{Ha}$. Sometimes the condition is even formulated as the assumption of $E = \text{Ha}$.^{8,53} By substitution into Eq. 20, k_L is eliminated and Φ becomes directly proportional to a_c :

$$\Phi = a_c A^* \sqrt{\frac{2}{m+1} D_A k (A^*)^{m-1} (B^0)^n} = a_c A^* \sqrt{D_A k_R} \quad (23)$$

with

Table 2. Main Characteristics of the Methods Using the Danckwerts' Plot to Determine a_e

Source	Packing	Gas	Liquid
Danckwerts and Gillham ⁶⁰	Raschig rings	Pure CO ₂ (saturated with water vapor)	K ₂ CO ₃ + KHCO ₃ + NaOCl (aq) NaOH + Na ₂ SO ₄ (aq) Na ₂ SO ₄ (aq)
Jhaveri and Sharma ²⁹	Raschig rings	O ₂ of the air	CuCl + HCl (aq)
Joosten and Danckwerts ²²	Raschig rings, Intalox saddles	Pure CO ₂	KHCO ₃ + K ₂ CO ₃ + KAsO ₂ (aq)
Rizzuti et al. ^{37,61}	Raschig rings	Pure CO ₂	K ₂ CO ₃ + KHCO ₃ + KAsO ₂ + sugar (aq)
Rizzuti and Brucato ⁶²			
Alper ³⁵	Fenske helices, porous ceramic cylinders	Pure CO ₂	K ₂ CO ₃ + KHCO ₃ + KAsO ₂ (aq)
Benadda et al. ⁴²	Raschig rings	CO ₂ (10%)	Na ₂ CO ₃ + NaHCO ₃ + NaOCl (aq)
Roesler and Raynal ⁶³	SMV8X	CO ₂ (10%)	Na ₂ CO ₃ + NaHCO ₃ + NaOCl (aq)

$$k_R = \frac{2}{m+1} k(A^*)^{m-1} (B^0)^n \quad (24)$$

representing the reaction term. So then, the effective area is given as:

$$a_e = \frac{\Phi}{A^* \sqrt{D_A k_R}} \quad (25)$$

To determine a_e experimentally, the rate of absorption per unit volume Φ is obtained by measuring the solute concentration changes under various operating conditions, while the other parameters are obtained from different sources. If the kinetics parameters are known, k_R can be calculated, otherwise, it can be determined in model apparatus, such as wetted-wall columns, non-aerated reactors,^{33,34} stirred cells, or jet apparatus.²⁹ In selecting the chemical system and reactant composition, caution must be exercised to verify that k_R is not too high so as to induce gas-side resistance. However, if this is the case, methods have been described to take into account this additional factor⁵² as described in the section "Determination of the Gas-Side Mass-Transfer Coefficient—Chemical absorption."

Chemical Systems. For fast pseudo- m th order reactions, the most popular system used is the chemical absorption of CO₂ into a liquid solution of NaOH (Table 1). This system has two main advantages: the kinetics and physical parameters are well established⁵⁹ and the components are readily available. The absorption of the CO₂ naturally in air is a particularly practical solution. As shown in Table 1, in recent years researchers have used this system exclusively.

Other chemical systems applied in the past have included the absorption of CO₂ into other reagents (KOH, amines), or of O₂ into solutions of dithionite, sodium sulfite with CoSO₄ as catalyst, and CuCl. In some of these systems, the reaction order may change with reactant concentration; this is the case with O₂ and sulfites,³¹ with which the order can range from 1 to 2. Deckwer⁵⁸ and Henriques de Brito et al.⁴¹ discourage the use of this last system, because of kinetic rate uncertainties. Alper,³⁵ however minimized uncertainties and achieved sufficient accuracy with this system by performing kinetic measurements in a stirred cell with liquid samples for each of his absorption runs. Sharma and Danckwerts¹² recommend the use of the absorption of CO₂ into NaOH, KOH, or amines, although they warn about gas-side resistance becoming non-negligible. They state that the use of NaOH or KOH is very convenient. For laboratory use, they also propose the absorption of O₂ into solutions of CuCl and dithionite. The system O₂–CuCl is, however, corrosive.

The constraints on the reaction speed need to be assessed over the whole column even for well-known absorption

systems. For example, Alix and Raynal⁵² found that the constraints are not fully met for the absorption of CO₂ diluted with air into 1 N NaOH solution due to appreciable gas-side resistance. To avoid this problem, they suggest using a more dilute system with only a 0.1 N NaOH solution to reduce gas-side resistance and only the CO₂ of air to avoid excessively loading the liquid solution.

The use of pure solute in the gas phase eliminates the gas-side mass transfer resistance. Most often, however, the solute gases are diluted mixed with a carrier gas, typically air. Gas-side resistance then exists, but usually contributes to only a few percent of the total resistance. Its impact can be taken into account if known from independent measurements or from appropriate literature correlations, a frequently applied option, or, if the system is in the intermediate regime, by using a variant of Danckwerts' plot.¹²

Danckwerts' Plot (Intermediate Reaction Regime): Methodology. If the reaction is in the intermediate reaction regime, that is, the condition $E > 9$ or $E > 5$ is not met, then the so-called Danckwerts' plot method can be used. Studies using this approach are listed in Table 2. The approximation of E as $E = \sqrt{(1 + \text{Ha}^2)}$ leads to the following expression for the volumetric flux of solute:

$$\Phi = k_L a_e A^* \sqrt{1 + \frac{D_A k_R}{k_L^2}} \quad (26)$$

which can be squared to give:

$$\Phi^2 = (k_L a_e A^*)^2 + D_A (a_e A^*)^2 k_R \quad (27)$$

The Danckwerts' plot then shows Φ^2 against k_R as a straight line, with $(k_L a_e A^*)^2$ as the intercept and $(a_e A^*)^2 D_A$ as the slope which then yield k_L and a_e . The reaction rate k_R can be varied by either changing the concentration of B or of a catalytic agent. The use of a catalyst has the advantage of keeping constant the physical properties of the system. A version of the method can be applied even if the gas-side resistance is not negligible.^{13,42} The uncertainty of the intercept is always greater than that of the slope, so the error of k_L is higher than that of a_e .

Chemical System. Systems for the intermediate reaction regime include the absorption of CO₂ into sodium or potassium bicarbonate buffer solutions, with either NaOCl or KAsO₂ as catalysts (Table 2). Danckwerts and Sharma⁶⁴ also mentioned formaldehyde as potential catalyst. The catalyst concentration is varied to create the Danckwerts' plot. Jhaveri and Sharma²⁹ noted that under certain conditions, the reaction of O₂ and CuCl can fall in this regime as well. The work of Rizzuti^{37,61,62} applied a potassium bicarbonate buffer with

Table 3. Main Details of Other Methods Using Chemical Absorption to Determine a_e

Source	Packing	Gas	Liquid	Principle
Danckwerts and Gillham ⁶⁰	Raschig rings	Pure CO ₂ (saturated with water vapor)	K ₂ CO ₃ + KHCO ₃ + NaOCl (aq) NaOH + Na ₂ SO ₄ (aq) Na ₂ SO ₄ (aq) NaOH (aq)	Analogy with stirred cell
Benadda et al. ²⁴	Berl saddles	CO ₂ in N ₂	NaOH (aq)	Regressed as model parameter
Nakov ⁶⁸	Honeycomb	NH ₃	H ₂ SO ₄ + sugar (aq)	Gas-film control, comparison with complete wetting
Aroonwilas and Veawab ²⁵	Sulzer DX	CO ₂ in N ₂	various amines	Regressed as model parameter

KAsO₂ in a the packed column operated without gas outlet. This is a convenient method to measure the amount of absorbed gas, as it will be equal to the inlet gas flow, however, it assumes that the gas flow rate has no effect on a_e . Several investigators consider this assumption to be valid below the flooding point.² Others indicate that the gas flow rate may have an effect (e.g., Weisman and Bonilla⁶⁵; Nakajima et al.⁴⁴; Alix et al.,⁵³ the correlations of Shulman et al.⁶⁶ and Bravo and Fair⁶⁷).

Other methods

In this section, less common chemical absorption methods are briefly reviewed as listed in Table 3.

Danckwerts and Gillham⁶⁰ used the stirred cell by analogy to a packed column with pure CO₂ to remove gas-side resistance. In the stirred cell, gas is absorbed into the liquid through a known flat interfacial area given by the horizontal cross-section of the cell. The validity of this analogy assumption was later verified with a maximum uncertainty of 14% by a first-order reaction method. Gas continuously flows through the cell while the liquid may or may not be renewed. The stirrer is positioned such that the bottom edge of the blades skims the liquid surface. The authors made absorption measurements both into reacting and into CO₂-free inert solutions. The ratio of the absorption rates:

$$\gamma_{DG} = \frac{\text{Rate of absorption into reacting solution}}{\text{Rate of absorption into CO}_2\text{-free inert solution}} = \frac{Ek_L(A^* - A^0)}{k_L A^*} \quad (28)$$

is evaluated for the cell as a function of stirring speed. The chemical systems used, bicarbonate buffer or NaOH, ensured that A^0 , the concentration of CO₂ in the bulk liquid, was null

leading to a common absorption driving force A^* in the numerator and denominator of Eq. 28 such that γ_{DG} becomes equal to E . The value of E depends on k_L and on the nature of the reactive solution. The authors therefore assumed that when the cell and the column have equal values of E , then they also have equal values of k_L . For a given stirring speed, k_L was calculated for the cell by knowledge of its interfacial area. The liquid flow rate of the packed column was then varied to obtain the same E . Under this condition, a_e can be calculated by dividing the volumetric mass-transfer coefficient $k_L a_e$ with the k_L of the cell. The calculation procedure is illustrated in Figure 4.

The method of Nakov⁶⁸ differs fundamentally from those presented above. The system, absorption of NH₃ into sulfuric acid is gas-side controlled. The method is based upon the fact that in this case, the effect of liquid flow rate on k_G is negligible at low values of liquid superficial velocities. By further assuming that the packing is completely wetted above a given liquid flow rate, a_e can be calculated from:

$$\frac{a_e}{a_g} = \frac{k_G a}{(k_G a)_L} \quad (29)$$

where $(k_G a)_L$ is the volumetric mass-transfer coefficient at the liquid superficial velocity corresponding to completely wetted packing. The drawback of the method is that it implicitly assumes that the absorption occurs only on the surface of the packing, and not in liquid elements between packings.

Recent approaches to determine a_e consist in developing more complete models of packed columns than the simpler expressions relating the global measured concentrations to the global mass transfer parameters. With these models, the parameter a_e is determined by varying its value to match the calculated solute concentrations to the experimental ones.^{24,25}

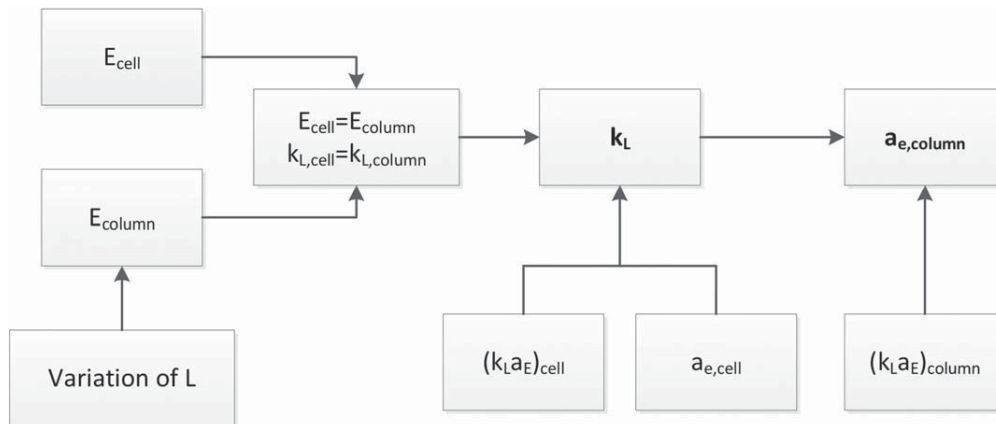


Figure 4. The calculation procedure of Danckwerts and Gillham⁶⁰ for the determination of a_e and k_L .

Table 4. Main Details of the Methods Using Physical Absorption to Determine a_e

Source	Packing	Gas	Liquid	Principle
Yoshida and Koyanagi ⁷³	Raschig rings, Berl saddles, spheres	Pure CO ₂ (saturated with absorbent)	Water Methanol	Analogy with bead column
Hikita et al. ⁷⁴	Raschig rings, Berl saddles	Pure CO ₂	Water Sugar (aq) Methanol (aq) Methanol	Analogy with single piece of packing
Yoshida and Koyanagi ⁷¹	Raschig rings	Methanol in air	Water	Comparison with packed column of fully wetted packing

The model of Benadda et al.²⁴ takes the effect of axial dispersion into account. The rigorous model of Aroonwilas and Veawab²⁵ accounts for heat of absorption, solvent evaporation, and simultaneous heat and mass transfer. Rejl et al.⁶⁹ proposed a “profile method,” where not only inlet and outlet concentrations, but also the concentration profiles are compared to the model results, although it was applied only for distillation. These methods allow relaxing experimental operating constraints required for the simpler “ideal” systems and open up alternatives. A small disadvantage of this method is that a more complex model has to be developed or adapted.

Evaporation

The method using evaporation (vaporization) of a pure liquid to determine a_e compares the volumetric mass-transfer coefficient $k_G a_e$ measured in a packed column to that measured in a second packed column filled with a packing of the same geometry but made of a porous material to ensure complete wetting. It assumes that the values of k_G are equal if the packings and the experimental conditions are identical. The wetted area of the porous packings equals the geometric area a_g and allows to calculate k_G . The unknown a_e of the first column, which will be smaller than the a_g due to incomplete wetting, is then obtained by dividing the measured volumetric mass-transfer coefficient by k_G . Weisman and Bonilla⁶⁵ used spheres as packing, and compared their results to those of Gamson et al.⁷⁰ under the same Reynolds number (Re_G) and liquid flow rate. Yoshida and Koyanagi⁷¹ applied the technique with Raschig rings, and made comparisons to data from Taecker and Hougen,⁷² by assuming that k_G values were identical in the two columns for the same Reynolds (Re_G) and Schmidt (Sc_G) numbers. The packings of Taecker and Hougen⁷² were made of a special clay-kieselguhr mixture having high porosity and capillarity, thus ensuring complete wetting. Both Gamson et al.⁷⁰ and Taecker and Hougen⁷² applied water flow only to saturate the packings with water and then varied the air flow rate to measure $k_G a_e$. Since in this case liquid was present only on the surface of the packings, the effective interfacial area was equal to the known wetted area.

This method can determine the effective area which equals the interfacial area for an evaporation process. The necessity to first measure the k_G and to apply special, custom-made packings is clearly penalizing particularly in the case of thin structures.

Physical absorption

The methods relying on physical absorption of a gas constituent in a liquid calculate the effective area by dividing the volumetric mass-transfer coefficient with either k_G or k_L . The value of the latter must first be determined by measuring the volumetric mass-transfer coefficient in another apparatus

having a well-defined effective interfacial area under conditions that ensure the equality of k_G or k_L between the two apparatus. Meeting this last constraint is the main difficulty. In the case of chemical absorption, it was reached by matching the enhancement factor E as presented earlier in Figure 4. The other apparatus can be a packed column with fully wetted packings, as in the case of evaporation (sections “Determination of the Effective Interfacial Area—Evaporation” and “Determination of the Effective Interfacial Area—Physical absorption—Comparison to a packed column with fully wetted packing”), or a device with largely different hydrodynamics in which case, the term “analogy” is used to describe the methodology (section “Determination of the Effective Interfacial Area—Physical absorption—Analogy between a packed column and another apparatus”). The articles using the method of physical absorption are listed in Table 4.

Comparison to a Packed Column with Fully Wetted Packing. The determination of a_e by comparing two packed columns one of which has a fully wetted packing was applied by Yoshida and Koyanagi⁷¹ with both vaporization (section “Determination of the Effective Interfacial Area—Evaporation”) and physical absorption. The mass-transfer coefficient k_G was used for the analogy. Methanol vapor was absorbed from air into water with Raschig rings as packing, and the results were compared to those of Taecker and Hougen⁷² at the same Re_G and Sc_G , as described in the section “Determination of the Effective Interfacial Area—Evaporation.” With this procedure, the effective interfacial area of the given process (evaporation or physical absorption) is obtained. The disadvantage is the need for a special porous packing of the same geometry.

Analogy Between a Packed Column and Another Apparatus. The principle of the method of analogy is that even though the other apparatus may be significantly different from a packed column, if the conditions of the analogy are met, which means the equality of one or more parameters, the mass-transfer coefficients will be equal. Two types of devices have been used for this type of analogy (Table 4), one consisting of a single piece of packing,⁷⁴ and the other of a bead column.⁷³ The gas phase was pure CO₂ in both papers, meaning that there is no resistance in the gas film, and the coefficient k_L was used for the analogy. Different liquids were applied to study the influence of physico-chemical properties on mass transfer parameters. In Hikita et al.,⁷⁴ who used a single piece packing with known surface,⁷⁵ the condition of analogy was the equality of liquid-side Reynolds numbers. The bead column is a vertical row of spheres, drilled through and connected by a stainless steel wire. The spheres are separated by short distances, and their surface is considered to be fully wetted. According to Yoshida and Koyanagi,⁷³ three parameters have

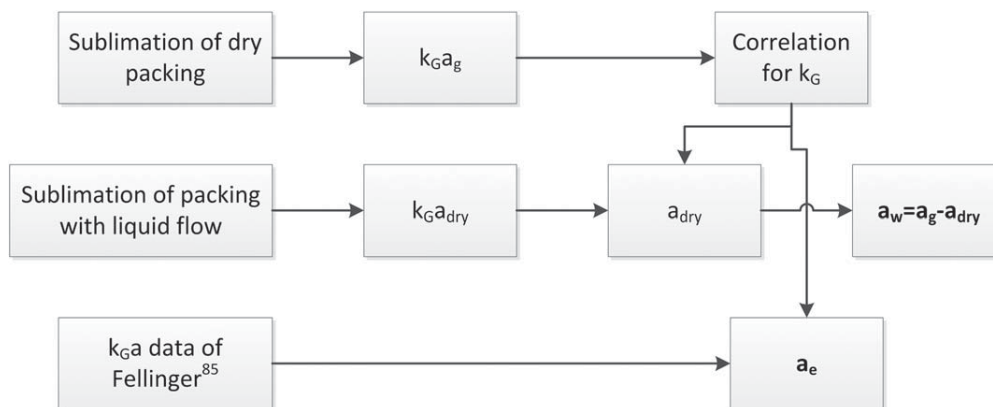


Figure 5. Calculation procedure to determine a_w and a_e with the method of the sublimation of the packing.

to be identical for the equality of k_L : (1) Re_L is based on the effective part of the liquid stream, (2) the number of times and degree of mixing of liquid streams, (3) the distance travelled over each packing piece by the liquid. Conditions 2 and 3 are fulfilled if the spheres of the bead column have the same size as the packing elements in the packed column, and the number of spheres equals the calculated number of packing pieces in the vertical direction of the packed column. The liquid flow rates of the two columns are adjusted so as to have the same number of transfer units, and according to the assumption, the same Re_L . For both columns, Re_L includes the effective wetted periphery, which contains the unknown a_e for packed column, but which is known from the sphere size for the bead column. An expression for a_e can be derived from the equality of Reynolds numbers.

The method of analogy can determine the effective interfacial area of physical absorption, but its disadvantage is that another apparatus is required, and the validity of the analogy has to be checked before applying the method.

Tomography

A new and promising method is the application of tomography, which makes it possible to visualize the inside of a column even under operation. Although tomography has been used to study packed columns, for example, to determine liquid hold-ups or observe gas and liquid distribution,⁷⁶ to the best of our knowledge, the method has only been applied for the determination of the wetted area in two research groups at the University of Texas at Austin^{49,77} and at the Université de Liège.^{54,78} Both groups used x-rays that are capable of passing through metal sheets and of providing a spatial accuracy of around 300 μm . Air and water were used on Mellapak 250.Y and 500.Y packings in the case of Green, and on Katapak SP2 and Mellapak 752.Y in the case of Aferka. The column was rotated while the x-ray source and detectors were fixed. There is no mention to what extent the rotation alters the flow patterns and the value of the wetted area. Green determined the wetted area by setting a threshold greyscale value for pixels, so that the calculated iso-surface would be the surface separating the gas and liquid phase. Aferka counted the pixels containing liquid in contact with the gas phase. The results of both authors were reported to agree with values of a_e obtained by chemical absorption method within less than 3%.

As compared to other methods that measure the wetted area, x-ray tomography provides a more physical evaluation

since it is based on a visualization technique. The uncertainty limit is determined by the resolution of the tomograph. The equipment for using this method is however not readily accessible to researchers owing to high costs and requirements for dedicated scanning bay with containment walls to shield radiation.

Colorimetry

In this method, a dye is added to the liquid phase that will color the packing surfaces with which it comes into contact. The wetted area is simply determined by measuring the total dyed surface. The method was first used by Mayo et al.,⁷⁹ which is also among the very first papers dealing with the determination of interfacial area in packed columns. Paper-made Raschig rings were used as packing material. The method was later applied by several Japanese authors,^{80,81} including Onda et al.⁸² and Choi and Kim⁸³ used both ceramic and paper-made Raschig rings. The problem with colorimetry is that it leads to overestimated wetted areas due to fluctuations of the liquid flow pathways that generate a dyed packing surface that is greater than the instantaneous wetted area. Moreover, the wettability of paper is different than for the material of commercial packings. The method is not convenient experimentally as it requires changing the bed at every condition and making visual evaluations of the dyed areas. Finally, its application to packing materials other than ceramic is uncertain.

Packing sublimation

The sublimation of the packing is a method that was used by the group of Shulman.^{20,84} The packings (Raschig rings and Berl saddles) were specially made from naphthalene, and they were sublimated into a gas stream, first without the presence of liquid phase, and then under different water flow rates.

Figure 5 presents the process to calculate a_w and a_e . By measuring the concentration in the outlet gas, $k_G a_g$ is determined, since the entire surface of the packing is sublimating. If the measurement is performed at various gas flow rates, and by knowing the value of a_g , a correlation for k_G can be obtained. When the experiments are repeated with liquid flow sublimation takes place only on the dry surfaces. The correlation for k_G then allows calculating the dry area, and the wetted surface area is obtained by difference with the total area. This calculation method assumes that the presence of the liquid phase does not change the nature of the gas flow. Finally, it is

possible to determine a_e , from volumetric mass-transfer coefficients measured by absorption (or vaporization) with the assumption that the k_G values of the sublimation and absorption experiments are identical under the same operating conditions. Shulman uses the volumetric mass-transfer coefficients of Fellingner⁸⁵ measured by absorption of ammonia into water.

The sublimation method can determine the wetted surface area and since it gives k_G , it can indirectly allow deriving the effective surface area of an arbitrary gas–liquid mass transfer process. However, it requires custom-made packings, which greatly impedes its use, especially if we consider thin structured or modern random packings, and the wettability may not be representative. Moreover, the parameter k_G is assumed to be independent of liquid load.

Conclusion

A variety of methods with different measurement principles are described in the literature for the determination of gas–liquid interfacial area in packed columns. As there are different concepts of interfacial area, such as wetted and effective interfacial area, and because the value of effective interfacial area depends on the nature of the mass transfer process, it is important to be aware what each method measures. This information is given in Table 5.

The method of chemical absorption can determine the effective interfacial area, which may be equal to the interfacial area, provided that the rate of absorption does not locally lead to saturation of the liquid phase. The most popular method is to use a fast, irreversible pseudo-first order reaction, most often that of CO_2 and NaOH , with negligible resistance in the gas phase, as under these conditions, the mass transfer rate becomes independent of k_L , and the interfacial area can be directly calculated. For the successful use of this method, one has to know the kinetics of the reaction, the physical properties of the system, and verify that the system is under appropriate fast reaction regime over the full range of conditions covered in the experiments. The system using CO_2 absorption (from air) into dilute NaOH solutions which meets the required constraints over a wide range of operating conditions and packing materials, making it a recommended method. A further advantage is that the reactants are readily available with little innuity.

Methods based on physical absorption and vaporization of pure liquids require analogy to other apparatus, or comparison with another packed column using fully wetted packings. The validity of analogy is a critical issue to determine whether or not the results will be accurate. They further can require preparing porous, fully wetted alternatives of packings, which is either cumbersome or impossible, therefore these methods are not recommended. Colorimetry or packing sublimation is not recommended either as the former overestimates a_w while the latter requires special packings. A new and promising method is tomography, which allows determining a_i directly. However, it requires sophisticated equipment.

Table 5. Types of Area Measured by Different Methods

Method	Area
Chemical absorption	$a_e (\leq a_i)$
Vaporization	$a_e = a_i$
Physical absorption	$a_e = a_{\text{dyn}}$
Tomography	a_w
Colorimetry	a_w
Sublimation	a_w, a_e

Determination of the Gas-Side Mass-Transfer Coefficient

All methods described in the literature provide a column averaged volumetric mass-transfer coefficient $k_G a$. Local values of k_G cannot be determined directly as techniques for measuring local concentrations in the gas or liquid film are not currently available. In many cases, the liquid-side mass transfer resistance is negligible in which case the process is controlled solely by $k_G a$. In theory, this condition holds only when the liquid phase is a pure substance. In every other situation, liquid-side resistance is more or less present, to an extent that depends on the system and on the gas and liquid flow rates. As discussed earlier (section “Determination of the Effective Interfacial Area—Specific areas defined in packings”), k_G can be calculated if a_e is known for the type of mass transfer process with which $k_G a_e$ was obtained. For example, a vaporization process will need a_i , whereas a physical absorption process where stagnant liquid areas may be saturated requires a_{dyn} . The methods for determining the gas-side mass-transfer coefficient can be classified into the following groups based on the principle of the measurement:

- vaporization of a pure liquid,
- physical absorption (and desorption),
- chemical absorption.

In the next sections, the methods found in the literature are presented, and the advantages and drawbacks of each group of methods are discussed.

Vaporization

In this method, a pure liquid is vaporized into a gas stream, and since no liquid-side resistance exists, it may seem to be a straightforward choice. The column should operate close to the state of adiabatic saturation in order to minimize the temperature gradients generated from the evaporative cooling of the liquid phase as these will significantly affect the interfacial vapor partial pressures that control the mass transfer driving force. In the majority of the experiments, this state is achieved by recirculating the liquid, and performing the measurement when its temperature is sufficiently stable in which case it is close to the adiabatic saturation temperature. An alternative^{71,86,87} consists in modifying the temperature of the inlet liquid to minimize the temperature difference between the inlet and the outlet. Another problem with the method is that the height of packed bed by which vapor saturation is reached in the gas phase is relatively short,⁸⁸ because $k_G a$ is high relative to the gas superficial velocity at the operating conditions commonly used. When saturation is approached, the results become more sensitive to measurement errors due to increased uncertainties in evaluating the driving force at the top of the column. However, with shorter packed beds, the contribution of the end-effects becomes more pronounced as the gas and liquid distribution within the packings may not have time enough to become fully established and representative of those in industrial columns.

The studies that have applied the method of vaporization are listed in Table 6. The method was particularly popular in the 40s and 50s. The gas phase was air in the majority of cases with some exceptions where He, CO_2 , or Freon-12 (dichlorodifluoromethane) were used to study the effect of the physical properties of the gas. In some investigations where the gas was not air, it was recirculated^{87,93} with partial moisture removal by condensation. An initial moisture content can be advantageous, as it prevents from reaching a low adiabatic

Table 6. Main Features of the Methods Using the Vaporization of a Pure Liquid to Determine k_G

Source	Packing	Gas	Liquid (pure constituents)
Sherwood and Holloway ⁸⁸	Raschig rings	Air	Water Methanol Benzene Toluene
Van Krevelen et al. ⁸⁹	Rings, spheres	Air	Water
McAdams et al. ⁹⁰	Raschig rings	Air	Water
Surosky and Dodge ⁹¹	Rings	Air	Water Methanol Benzene Ethyl n-butanoate
Weisman and Bonilla ⁶⁵	Spheres	Air	Water
Yoshida and Tanaka ^{92*}	Raschig rings	Air	Water
Hensel and Treybal ⁸⁶	Berl saddles	Air	Water
Lynch and Wilke ⁸⁷	Raschig rings	Air He Freon-12	Water
Yoshida ⁹³	Raschig rings	Air He CO ₂	Water
Shulman and Delaney ⁹⁴	Raschig rings	Air + CCl ₄	CCl ₄
Shulman and Robinson ^{95*}	Raschig rings	Air + CCl ₄	CCl ₄
Yoshida and Koyanagi ⁷¹	Raschig rings	Air	Water
Shulman et al. ²¹	Raschig rings	Air	Water
Vidwans and Sharma ²⁸	Raschig rings	Air He Freon-12	Triethylamine
Onda et al. ⁹⁶	Raschig rings, Berl saddles, spheres	Air	Water
Alix et al. ⁵³	4D	Air	Water

*Partially or entirely dehumidification.

saturation temperature and reduces undesired heat transfer with the environment. In cases where the gas phase was air, it was generally drawn directly from the atmosphere. In some studies, the air was actually dried before entering the column while in others⁵³ the air was actually humidified by water evaporation in a preheater.

The evaporated liquid has usually been water as it is the simplest option. A number of organic liquids have been used as well. Sherwood and Holloway⁸⁸ and Surosky and Dodge⁹¹ studied the effect of vapor diffusivity on k_{Ga} and found a power law dependency of $D^{0.17}$ and $D^{0.15}$, respectively. The values of these exponents are much lower than those generally proposed by correlations for k_G which range between 1/2 and 2/3.² Sherwood and Holloway⁸⁸ and Surosky and Dodge⁹¹ concluded that eddy diffusivity plays an important role in establishing the gas-side mass transfer rate, but they did not consider the effect of liquid properties on a_c (especially surface tension), which may have led to underestimated diffusivity exponents. Shulman and Delaney⁹⁴ vaporized CCl₄ into air already containing the substance at different concentration levels in order to study the effect of p_{BM} , the mean partial pressure of the inert carrier gas. In addition, using CCl₄ instead of water makes it possible to obtain more generally valid correlations, as the physical properties of the gas phase change to a greater extent with concentration.⁹⁵ For example, Sc_G shows a fivefold variation with CCl₄ mole fraction ranging from 0 to 0.7 in air.

The mass transfer driving force includes the equilibrium concentration of the liquid constituent in the gas phase at the adiabatic saturation temperature, which is assumed to be the liquid temperature. The precision of the temperature measurement is therefore critical for determining the k_{Ga} : a 1°C difference at 20°C causes a 6% change in the vapor pressure of water. If the system is within 20% of saturation, this can represent a 30% uncertainty in k_{Ga} . If the liquid phase is other than

water, chemical analysis of the gas phase is required, instead of the simpler humidity measurement.

The reverse process, dehumidification, or condensation, has also been used as a method for determining k_{Ga} . Yoshida and Tanaka⁹² and Shulman and Robinson⁹⁵ performed such tests, where the solute content of air was reduced by getting it into contact with a cold liquid stream, thus partially condensing the vapor. The correlations established for vaporization can only be applied here with a precise measurement or a rigorous estimation⁹⁵ of interfacial temperature. With dehumidification, the temperature of the liquid surface differs from that of the bulk liquid, as heat transfer takes place in the liquid, unlike the case of constant liquid temperature vaporization, where the constant liquid temperature means that vaporization heat is provided entirely by the gas phase.⁹² For this reason, dehumidification is not a practical alternative to vaporization.

Vaporization of a pure liquid, especially if air and water are used, is a practical method to determine k_{Ga} . The liquid phase offers no resistance, and if the liquid is water, only the temperature and humidity measurements are needed with no use of other chemicals or chemical analysis. However, the water temperature stability must be ensured, preferably within $\pm 0.2^\circ\text{C}$, in order to minimize the heat transfer in the liquid phase and resulting uncertainties in the evaluation of the driving force. Moreover, the packed bed height must be kept low enough to avoid getting close to saturation which otherwise also induces driving force uncertainties.

Physical absorption

The method of physical absorption relies on using a solute of very high solubility in the liquid so as to minimize liquid-side resistance and sensitize the absorption flux only to the gas side mass-transfer coefficient. In most cases, the liquid-side resistance, although low, is not negligible, which requires some means of assessing its value in order to calculate k_{Ga} .

Table 7. Main Characteristics of the Methods Using Physical Absorption to Determine k_G

Source	Packing	Gas	Liquid	Method
Dwyer and Dodge ¹⁰⁵	Raschig rings	NH ₃ in air	Water	$k_L a_e$ subtracted from $K_G a_e$
Othmer and Scheibel ¹⁰²	Raschig rings	Acetone in air	Water	Assumption 1 + 2
White and Othmer ¹⁰³	Stedman triangular pyramid	Acetone in air	Water	Assumption 1 + 2
Molstad et al. ¹⁰⁷	Raschig rings, Berl saddles, spiral rings, partition rings, drip-point ceramic grids, wood grids	NH ₃ in air	Water	$k_L a_e$ subtracted from $K_G a_e$
Scheibel and Othmer ¹⁰⁴	Raschig rings	Acetone in air	Water	Assumption 1 + 2
Gross and Simmons ¹⁰⁶	Berl saddles	Butanone in air Benzene in air Trichloroethylene in air Chloroform in air	Kerosene	Liquid-side resistance was neglected
Van Krevelen et al. ⁸⁹	Rings, spheres	NH ₃	Water	Assumption 1 + 2
Landau et al. ¹⁰⁸	Raschig rings	NH ₃ in N ₂ UF ₆ in N ₂	Water Heavy oil	$k_L a_e$ subtracted from $K_G a_e$ Assumption 1
Hutchings et al. ¹⁰⁹	Raschig rings	Acetone in air	Water	Assumption 1 + 2
Whitney and Vivian ⁹⁹	Raschig rings	SO ₂	Water	Assumption 1
Molstad and Parsly ¹¹⁰	Drip-point ceramic grids	NH ₃ in air	Water	$k_L a_e$ subtracted from $K_G a_e$
Houston and Walker ¹¹¹	Raschig rings	NH ₃ in air Acetone in air Methanol in air Ethanol in air	Water	$k_L a_e$ subtracted from $K_G a_e$
Zabban and Dodge ¹¹²	Raschig rings, Berl saddles	Acetone in air Methanol in air	Water	$k_L a_e$ subtracted from $K_G a_e$
Onda et al. ¹¹³	Raschig rings, Berl saddles, spheres	NH ₃ in N ₂	Water	$k_L a_e$ subtracted from $K_G a_e$
Yoshida and Koyanagi ⁷¹	Raschig rings	Methanol in air	Water	Liquid-side resistance was neglected
Shulman et al. ²¹	Raschig rings	Methanol in air	Water	$k_L a_e$ subtracted from $K_G a_e$
Billet and Maćkowiak ¹¹⁴	Pall, Impulse type 50	NH ₃ in air	Water	$k_L a_e$ subtracted from HTU _{OG}
Maćkowiak ¹¹⁵	Mellapak 250.Y, Montz B1, C1, Gempak 2A	NH ₃ in air	Water	$k_L a_e$ subtracted from HTU _{OG}
San-Valero et al. ¹¹⁶	Flexiring, PAS Winded Media	Isopropanol in air	Water	Liquid-side resistance was neglected

The relative magnitude of the two resistances also depends on the flow conditions for which a high L/G value is preferred to minimize the liquid-side resistance.

Literature sources use different approaches to obtain $k_G a_e$ from the overall coefficient $K_G a_e$. A common method consists in measuring independently the liquid-side resistance or estimating it with a correlation, and then subtracting it from the total mass transfer resistance. Numerous authors apply assumptions on the dependence of $k_G a_e$ and $k_L a_e$ on gas and liquid flow rates (G and L , respectively) to assess evolutions of their relative contributions with flow conditions. The independency of $k_L a_e$ to G (Assumption 1) is generally accepted to be true below the loading point. According to penetration theory, $k_L a_e$ does not depend on G . This has been confirmed experimentally such that the values of $k_L a_e$ recalculated from the correlations reviewed by Wang et al.² for k_L and a_e are independent of the gas flow rate. The experimental work of Murrieta et al.⁹⁷ showed that $k_L a_e$ did not change by varying G below the loading point, although Sherwood and Holloway⁹⁸ found an increase in the loading region. It is also known that a_e becomes dependent on G above the loading point. On the basis of the above, the gas-side total resistance can then be expressed as:

$$\frac{1}{K_G a_e} = \frac{1}{k_G a_e} + \frac{m}{k_L a_e} = \frac{1}{\beta G^q L^p} + \frac{m}{\alpha L^p} = \frac{m}{K_L a_e} \quad (30)$$

Whitney and Vivian⁹⁹ applied this equation, to determine and establish correlations for both $k_G a_e$ and $k_L a_e$. This was done by plotting $1/K_L a_e$ against $1/G^q$ at constant liquid flow rate.

The value of the exponent q was optimized to get the best linear fit. Repeating the procedure for several values of L , the intercepts ($1/\alpha L^p$) and slopes ($1/m\beta L^p$) of the lines were then plotted as a function of L , to determine the exponents p and r .

Several authors have assumed that the exponent q equals 0.8 (Assumption 2). This value was chosen on the basis of wetted-wall column investigations, and the work of Sherwood¹⁰⁰ who correlated the data of Kowalke et al.¹⁰¹ The overall mass transfer resistance is then:

$$\frac{1}{K_G a_e} = \frac{1}{\beta G^{0.8}} + \frac{m}{k_L a_e} \quad (31)$$

If $1/K_G a_e$ is measured at different gas flow rates and plotted against $1/G^{0.8}$, then the parameter β can be determined from the slope of the resulting straight line, leading to a correlation for $k_G a_e$ in the form of $k_G a_e = \beta G^{0.3}$. The liquid-side resistance can be calculated from the intercept. This method was used by the group of Othmer^{102–104} and by Van Krevelen et al.⁸⁹ for the separation of the gas- and liquid-side resistances.

The coefficient β can encompass the eventual dependence of $k_G a_e$ on L , as long as the measurements are performed at a constant L . If data at different liquid flow rates are used for the same line then $k_G a_e$ is assumed independent of L . Several authors (e.g., Dwyer and Dodge¹⁰⁵) indicate however that this assumption does not hold, because L can increase $k_G a_e$ by increasing turbulence in the gas film.

The validity of Assumption 2 is questionable as numerous other measurements have led to exponent values ranging between 0.5 and 1.² If the measurement points do not fall on a

line, it would indicate that the exponent is different from 0.8, but taking into account the measurement errors the conclusions are not trivial.

Gross and Simmons¹⁰⁶ neglected liquid-side resistance on the basis that none of the parameters of the equation

$$K_G a_e = \alpha G^\gamma \quad (32)$$

seemed to depend on the liquid flow rate.

Table 7 lists the main experimental characteristics of articles using the physical absorption method along with assumptions for treating the data. The method was popular up into the 60s; with the first experiments performed in the 40s.

In some cases,^{21,99,105} the gas phase was humidified before entering the absorption column. This measure was taken to reduce any unwanted temperature drop from water evaporation in the absorption column, which would alter the measured $k_G a_e$. The evaporation of water can also directly hinder the diffusion of the solute, which proceeds in the opposite direction. The only author to investigate the measurement error caused by the water evaporation was Dwyer and Dodge¹⁰⁵ who found the overall mass-transfer coefficient to be lower if the gas was humidified, but in most cases the difference fell within experimental uncertainty.

The various solutes have been NH_3 , organic solvents, such as acetone, methanol, ethanol, and isopropanol, or in one case,⁹⁹ SO_2 , and they were mixed to a carrier gas, air, or N_2 . The concentrations of solute in the inlet gas, when given, have generally ranged between 1 and 10 mol%. Lower values down to 0.12 mol% can be found in Scheibel and Othmer¹⁰⁴ and higher values up to 25 mol% have been used by Gross and Simmons,¹⁰⁶ Hutchings et al.¹⁰⁹, and Whitney and Vivian.⁹⁹ In the case of NH_3 absorption, Whitney and Vivian⁹⁹ specifically warned that although some authors neglected the liquid-side resistance, its contribution may be significant, sometimes reaching half of the total resistance at low L/G values. The liquid phase has generally been water, with the exception of Gross and Simmons¹⁰⁶ and Landau et al.¹⁰⁸ The latter investigated extreme conditions in terms of density, viscosity, diffusivity of the fluids using UF_6 absorption into a heavy oil (molar masses: 352 and 750 g/mol, respectively) at temperatures around 90°C in order to assess the extrapolability of correlations for design and calculation methods. Good agreement was obtained between experimental results and the values calculated using correlations for $k_G a$ and $k_L a$ (corrected for the changed physical properties). The authors used desorption data from the same system, as well.

The method of physical absorption has the advantage that no chemical reaction takes place, and that saturation of the liquid phase is usually not a problem. However, a fundamental problem is the existence of liquid-side resistance, the contribution of which should be assessed for every flow condition. In some cases, it may very well be negligible, but more often than not the liquid-side resistance in these systems has an impact that is increasingly important at lower values of L/G where $k_L a$ is smaller. When both resistances contribute significantly to the overall mass transfer rate, then $k_G a$ can be extracted from the data simultaneously with $k_L a$ provided that assumptions are made on the dependency of these parameters on G and L or that $k_L a_e$ can be independently evaluated by other means (experimental, correlations). When the liquid-side resistance is secondary to the overall resistance, the uncertainties in estimating $k_L a_e$ will not significantly affect the determined $k_G a_e$ values.

Chemical absorption

The liquid-side resistance can be eliminated or greatly reduced by a chemical reaction rapidly consuming the solute such that $K_G a_e = k_G a_e$, and k_G can be calculated by dividing with a_e . The reaction can be instantaneous or of finite speed, but must be very fast in order to eliminate the solute from the liquid film, and thus the liquid-side resistance.¹² The necessary condition for an instantaneous reaction is¹³:

$$\text{Ha} \gg E_{\text{inf}} \quad (33)$$

Danckwerts and Sharma⁶⁴ states that a 10-fold difference between Ha and E_{inf} is sufficient.

The reaction plane is the location in the liquid film where the instantaneous reaction takes place. If the following additional condition also holds:

$$k_G p < k_L \frac{D_A B^0}{D_B v} \quad (34)$$

then the reaction plane is at the interface which eliminates the liquid-side resistance. In the above expression, p is the partial pressure of the solute in the bulk gas phase. Sharma and Danckwerts¹² specify the above condition in the following forms for $v = 1$:

- for an instantaneous reaction by assuming equal diffusivities:

$$k_G p < k_L B^0 \quad (35)$$

- for a reaction of finite speed, where He is the Henry's law constant:

$$k_G \text{He} \ll k_L \text{Ha} \quad (36)$$

Suitable reactions are those of SO_2 , Cl_2 , or I_2 with NaOH , SO_2 with Na_2CO_3 and NH_3 or triethylamine (Et_3N) with H_2SO_4 .¹³ With these systems, the partial pressure of the solute at the interface is negligible. Applying these conditions to a packed column, Eq. 6 leads to an expression for k_G that is conveniently independent of thermochemical properties:

$$k_G = \frac{G}{\text{Ha}_e} \ln \left(\frac{y_{\text{in}}}{y_{\text{out}}} \right) \quad (37)$$

Table 8 lists the articles in which the method of chemical absorption has been used. Either an acidic solute, such as H_2S , SO_2 , or CO_2 , is absorbed into a basic solution (NH_3 for H_2S and NaOH for SO_2 and CO_2), or a basic solute, such as NH_3 is absorbed into an acid, typically H_2SO_4 . In recent years, the absorption of SO_2 into NaOH has become the most popular option. The carrier gas has almost always been air except in the work of Vidwans and Sharma,²⁸ where several freons were used as well, to study the effect of gas phase diffusivity.

The majority of the methods use instantaneous or very fast reactions. A specific alternative is described by Laurent et al.¹³ and used by Alix and Raynal.⁵² In this case, a fast reaction is used ($\text{CO}_2 + \text{NaOH}$), which satisfies the following conditions: $\text{Ha} \ll E_{\text{inf}}$ and $\text{Ha} > 5$. These are conditions close to those presented in the section "Determination of the Effective Interfacial Area—Chemical absorption—Fast reactions—Methodology" for the determination of a_e by a chemical method where the liquid-side resistance is independent of k_L and varies only with a_e . The difference in this case is that the gas-side resistance is not negligible because of a high NaOH

Table 8. Main Characteristics of Methods Using Chemical Absorption to Determine k_G

Source	Packing	Gas	Liquid
Fellinger ⁸⁵	Berl saddles	NH ₃ in air	H ₂ SO ₄ (aq)
Johnstone and Singh ¹¹⁷	Grids, plates, wire helices, Raschig rings, spiral rings	NH ₃ in air SO ₂ in air	Acetic acid (aq) NaOH (aq)
Van Krevelen et al. ¹¹⁸	Glass rings	H ₂ S in air	NH ₃ (aq) (NH ₄) ₂ SO ₄ (aq)
Vidwans and Sharma ²⁸	Raschig rings, Intalox saddles	NH ₃ in air NH ₃ in air or freons Et ₃ N in air or freons SO ₂ in air or freons Cl ₂ in air or freons	H ₂ SO ₄ (aq) Acetic acid (aq) NaOH (aq)
Weiland et al. ⁴⁰	Goodloe, Montz A2	SO ₂ in air	NaOH (aq)
Nakov and Kolev ¹¹⁹	Turbo-Pack	NH ₃ in air	H ₂ SO ₄ (aq)
Moucha et al. ¹²⁰	Modified Intalox saddles	SO ₂ in air	NaOH (aq)
Hoffmann et al. ⁸	Pall rings	SO ₂ in air	NaOH (aq)
Kim and Deshusses ¹²¹	Lava rocks, porous ceramic beads and Raschig rings, Pall rings, polyurethane foam	CO ₂ in air	NaOH (aq)
Alix and Raynal ⁵²	IMTP50	CO ₂ in air or of the air	NaOH (aq)
Wang et al. ^{55,56}	Mellapak 2X, 250.X, 250.Y, Flexipac, Raschig Super-Pak, Raschig Super-Ring, Pall rings, GT-Pak 350Y, 350Z	SO ₂ in air	NaOH (aq)
Rejl et al. ⁵⁷	Super-Pak 250.Y	SO ₂ in air	NaOH (aq)
Kunze et al. ¹⁰	Pall rings, Mellapak 250.Y	NH ₃ in air	H ₂ SO ₄ (aq)

concentration that leads to a CO₂ concentration gradient in the gas film by increased reaction rate. In this situation, a Danckwerts' plot method can be applied using the expression for the ratio of the partial pressure of the solute (p) and the volumetric rate of absorption (Φ). For a pseudo-first order reaction, this expression is:

$$\frac{p}{\Phi} = \frac{1}{k_G a_e} + \frac{He}{\sqrt{kDB^0} a_e} \quad (38)$$

The left-hand side can be plotted as a function of $He/\sqrt{kDB^0}$. The interfacial area is determined from the slope, $k_G a_e$ from the intercept. Although this method can be used to determine k_G , due to potentially large uncertainties in the determination of the intercept, it is better suited for taking into account gas-side resistance during the determination of a_e . Moreover, it is more labor intensive, as repeated experiments with different values of k or B^0 must be performed.

As regards liquid-side resistance, most authors have neglected it without verification but not all. Johnstone and Singh¹¹⁷ verified this assumption by plotting $1/K_G a_e$ as a function of $1/u_G^{0.8}$, where u_G is the superficial velocity of the gas. A straight line fitted to the measurement points was found to intercept the origin when extrapolated. At the origin $1/u_G^{0.8} = 0$, and $1/K_G a_e$ equals the liquid-side resistance according to Eq. 30. Thus, the fitted line passing through the origin is hinting to an inexistent liquid-side resistance. Vidwans and Sharma²⁸ studied the effect of L on both $k_G a_e$ and k_G and observed that the variation of $k_G a_e$ with L was entirely due to that of a_e , meaning that k_G was really the true gas-side mass-transfer coefficient. The system CO₂-NaOH⁵² stands apart from the rest, as the reaction belongs to the fast reaction regime, and the liquid-side resistance can be accounted for by the kinetics of the reaction system alone, but it requires more work. On the other hand, Kim and Deshusses¹²¹ treated this reaction as an instantaneous one, as they found no influence of the NaOH concentration on the absorption rate above a pH of 13.

Although only applied by Kunze et al.¹⁰ by recirculating the gas phase, Hoffmann et al.⁸ recommended to saturate the gas stream with water prior to absorption in order to avoid

temperature effects and multicomponent mass transfer due to the evaporation of water. The magnitude of the errors introduced was not discussed. The most important effect of the cooling down of air is possibly the change in gas-phase diffusivity. Sharma and Danckwerts,¹² among others, advised to always perform the calculation of $k_G a_e$ based on the measured gas phase concentrations, more precise than those of liquid phase.

Sherwood and Holloway⁸⁸ recommend the method of chemical absorption instead of vaporization of a pure liquid due to the potential experimental difficulties such as the necessity of short beds and careful control of liquid temperature. However, the packed bed height may be limited in this case as well, because the rapid consumption of the solute can lead to absolute residual values in the gas phase so small as to be within the uncertainty limits of practical analytical devices.

The main advantage of the method of chemical absorption is the near complete elimination of the liquid-side resistance, if the reaction fulfills the necessary criteria, so that the reaction takes place at the gas-liquid interface. Disadvantages are that chemical analysis is required, and that the packed bed height might be limited due to the depletion of the solute in the gas phase.

Conclusion

The methods used for the determination of $k_G a_e$ belong to one of the three following groups: vaporization of a pure liquid, physical absorption, or chemical absorption. Each of these aims to eliminate the liquid-side resistance or at least to reduce it to a value that can be safely neglected. If a pure liquid is vaporized, this is naturally accomplished. By physical absorption of a very soluble compound, the liquid-side resistance can be greatly reduced if appropriate G/L ratios are used. However, the liquid-side resistance, no matter how low, always exists, and it is suggested to check its magnitude either by a correlation or by using literature values. If the liquid-side resistance is not negligible, it is also possible to obtain $k_G a_e$ by subtracting $k_L a_e$ from the overall mass-transfer coefficient, or by separating the two resistances based on certain

assumptions. However, these approaches seem to be prone to include additional errors in $k_G a_e$. By chemical absorption, an instantaneous or very fast reaction ensures that the solute is consumed at the gas-liquid interface, eliminating the resistance from the liquid film. It is then necessary to check that the conditions set the system in the appropriate reaction regime.

From a practical point of view, each group of methods suffers from some type of disadvantage. In general, quick saturation or depletion of the gas phase limits the height of the packed bed that can be used due to uncertainties in analytical system for measuring relative concentration changes. By vaporization, the saturation value also contains experimental error, as it is calculated from measured liquid temperatures. Physical and chemical absorption require handling chemicals, and performing chemical analyses, yet another source of uncertainties, while the measurement of temperatures and humidities is sufficient for the vaporization of water.

Of these various methods, using chemical absorption in the instantaneous regime is recommended first as the results are independent of thermochemical properties, with choice reactions systems being air diluted SO_2 or NH_3 into NaOH or H_2SO_4 solutions respectively. If the nature of the chemicals is an issue then physical desorption is an option if k_L is known or is negligible, otherwise evaporation methods should be used.

Determination of the Liquid-Side Mass-Transfer Coefficient

As with gas-side mass-transfer coefficients, the methods described in the literature provide column averaged volumetric liquid-side mass-transfer coefficients $k_L a_e$. Local values cannot be determined directly as measurement techniques for local concentrations in the gas or liquid film are not currently available. It is generally assumed that the gas-side mass transfer resistance is negligible, and thus $K_L a_e = k_L a_e$. If the gas phase is pure, this assumption is entirely valid. Otherwise, gas-side resistance is present to a degree that depends on the chemical system as well as on the flow conditions. Once $k_L a_e$ has been measured, the value of k_L can be calculated by dividing by a_e for the type of mass transfer process used. To determine the liquid-side mass-transfer coefficient, the following groups of methods can be applied:

- physical absorption,
- desorption,
- chemical absorption.

In the next sections, the methods found in the literature are presented, and the advantages and drawbacks of each group of methods are discussed.

Physical absorption

Methods using physical absorption have been used extensively since the 1930s. Table 9 presents the literature using this principle, along with the chemical systems and basis of the determination of $k_L a_e$.

The majority of the methods use a solute gas component of very low solubility such that the mass transfer resistance lies predominantly within the liquid film while the gas-side resistance is negligible. However, low solubilities can lead to quick saturation of the liquid phase, a situation that induces large experimental uncertainties, and that can occur especially if the gas is purely the solute.²⁶ The dominance of liquid-side resistance will be favored at low L/G values.

When gases with high solubility are used then the gas-side resistance is not negligible, and should be obtained either from another means, or by simultaneous evaluation with $k_L a_e$. In the first case the liquid-side resistance, and thus $k_L a_e$ can be obtained by subtracting the gas-side resistance $1/k_G a_e$ from the measured overall resistance. Either $k_G a_e$ is measured by an appropriate method at the same conditions (e.g., Hoffmann et al.⁸) or it can be estimated from a correlation (e.g., Scheibel and Othmer¹⁰⁴) This procedure, however, is only correct if a_e is the same for the methods by which $k_G a_e$ and $k_L a_e$ were measured: for example, if $k_G a_e$ and a_e were measured by chemical absorption while $k_L a_e$ was determined by physical absorption, then an error is introduced into k_L .⁹ This is the case with the results of Hoffmann et al.⁸ who implicitly assume the equality of areas. This problem can be overcome by using the correct effective areas for each measurement:

$$\frac{1}{k_L} = \frac{(a_e)_L}{(K_L a_e)_L} - \frac{(a_e)_G}{m(k_G a_e)_G} \quad (39)$$

A disadvantage of measuring or estimating $k_G a_e$ separately is that its error is propagated to $k_L a_e$. The higher the gas-side resistance, the more important this effect. In the second case, the simultaneous determination of $k_G a_e$ and $k_L a_e$ can be obtained based on assumptions on their dependencies to gas and liquid flow rates (see the section “Determination of the Gas-Side Mass-Transfer Coefficient—Physical absorption”). It is generally assumed that $k_L a_e$ is independent of G (Assumption 1, Eq. 30), and, except for Whitney and Vivian,⁹⁹ that $k_G a_e$ is proportional to $G^{0.8}$ (Eq. 31). Although this method can be used to determine $k_L a_e$, it was used in the literature sources with the primary aim of obtaining $k_G a_e$ in measurements where the majority of the mass transfer resistance is located in the gas film with a secondary but non-negligible contribution of the liquid film resistance. This is not a recommended condition for $k_L a_e$ as the aim of this procedure is primarily the determination of $k_G a_e$, and although $k_L a_e$ is also obtained, it is likely to contain the greater part of measurement errors.

The most commonly used system has been the absorption of CO_2 in water. The CO_2 has often been pure, but also mixed into carrier gases such as air or N_2 at concentration between 3 and 15 mol%, or even up to 48 mol% in the case of Payne and Dodge.¹²² Laso et al.³ pointed out potential drawbacks of using CO_2 relative to other poorly soluble gases. First, the solubility of CO_2 is greater than that of O_2 , H_2 , or N_2 . Second, the absorption of CO_2 into water involves chemical reactions with the formation of carbonic acid, and although these should not normally influence the mass transfer rate, the presence of cations in non-demineralized water can have an effect. Third, if solid precipitations are formed with the cations, even in very low amounts, they may modify the wettability of the packing by adhering to its surface. Laso et al.³ performed desorption experiments, but their remarks are equally valid for absorption.

Some authors have used various aqueous solutions to study the effect of liquid properties, such as viscosity and surface tension. Organic solvents, most frequently methanol, were also applied with the same purpose. Van Krevelen et al.,¹¹⁸ Linek et al.,³⁹ Moucha et al.,¹²⁰ Kim and Deshusses¹²¹, and San-Valero et al.¹¹⁶ used the absorption of O_2 into water. Onda et al.,¹³¹ in addition to CO_2 , performed measurements of H_2 absorption into water to determine the dependency of $k_L a_e$ to Sc_L .

Table 9. Main Characteristics of the Methods Using Physical Absorption to Determine k_L

Source	Packing	Gas	Liquid	Principle
Payne and Dodge ¹²²	Rings	CO ₂ in air	Water	Gas-side resistance neglected
Data of Allen ¹²³ reported by Sherwood and Holloway ⁹⁸	Raschig rings	CO ₂	Water	Gas-side resistance neglected
Othmer and Scheibel ¹⁰²	Raschig rings	Acetone in air	Water	Assumption 1 + 2
White and Othmer ¹⁰³	Stedman triangular pyramid	Acetone in air	Water	Assumption 1 + 2
Scheibel and Othmer ¹⁰⁴	Raschig rings	Acetone in air Butanone in air Methyl isobutyl ketone in air 2-Heptanone in air	Water	Assumption 1 + 2 k_G subtracted from K_L
Van Krevelen and Hoftijzer ¹²⁴	Rings	O ₂	Aqueous suspension of Prussian white	Gas-side resistance neglected
Landau et al. ¹⁰⁸	Raschig rings	UF ₆ in N ₂	Heavy oil	Assumption 1
Van Krevelen et al. ¹¹⁸	Rings	NH ₃	Water	Assumption 1 + 2
Hutchings et al. ¹⁰⁹	Raschig rings	Acetone in air	Water	Assumption 1 + 2
Whitney and Vivian ⁹⁹	Raschig rings	SO ₂ (saturated with water)	Water	Assumption 1
Koch et al. ¹²⁵	Raschig rings	CO ₂ in air	Water	Gas-side resistance neglected
Hikita et al. ¹²⁶	Raschig rings, Berl saddles (stacked/dumped, with and without paraffin coating)	Pure CO ₂	Water	No gas-side resistance
Ueyama et al. ¹²⁷	Rings	Pure CO ₂	Water	No gas-side resistance
Fujita and Hayakawa ¹²⁸	Raschig rings, Berl saddles	Pure CO ₂	Water	No gas-side resistance
Yoshida and Koyanagi ⁷³	Raschig rings, Berl saddles, spheres	Pure CO ₂ (saturated with absorbent)	Water Methanol	No gas-side resistance
Onda et al. ¹²⁹	Raschig rings	Pure CO ₂	Water	No gas-side resistance
Hikita et al. ¹³⁰	Raschig rings	Pure CO ₂	Water	No gas-side resistance
Onda et al. ¹³¹	Raschig rings	Pure CO ₂	Water	No gas-side resistance
Onda and Sada ¹³²	Raschig rings	Pure H ₂ (saturated with absorbent) Pure CO ₂	Water Methanol Ethanol CCl ₄ Benzene Decaline	No gas-side resistance
Hikita et al. ⁷⁴	Raschig rings, Berl saddles	Pure CO ₂	Water Sugar (aq) Methanol (aq) Methanol	No gas-side resistance
Onda et al. ¹³³	Spheres	Pure CO ₂	Water	No gas-side resistance
De Waal and Beek ¹³⁴	Raschig rings	CO ₂ in air (saturated with water)	Water	Gas-side resistance neglected
Onda et al. ⁹⁶	Raschig rings, Berl saddles, spheres, rods	CO ₂	Water (+ surfactant) Methanol CCl ₄	No gas-side resistance No gas-side resistance
Merchuk et al. ¹³⁵	Raschig rings	Pure CO ₂	Water	No gas-side resistance
Sahay and Sharma ³²	Raschig rings, Pall rings, Intalox saddles	Pure CO ₂	Water	No gas-side resistance
Joosten and Danckwerts ²²	Raschig rings, Intalox saddles	Pure CO ₂	NaNO ₃ + sugar (aq)	No gas-side resistance
Maćkowiak ¹³⁶	Raschig rings, Bialecki rings, I-13 rings	CO ₂ in air	Water	Gas-side resistance neglected
Merchuk ³⁶	Raschig rings, flat rings, spirals, saddles	CO ₂ in air or in pure form	Water	Gas-side resistance neglected or no gas-side resistance
Mangers and Ponter ^{137,138}	Raschig rings	Pure CO ₂ (saturated with water)	Water Glycerol (aq)	No gas-side resistance
Billet and Maćkowiak ^{114,139}	Pall rings, NSW rings, Hiflow rings, Hacketts, Impulse type 50	CO ₂ in air	Water	Gas-side resistance neglected
Linek et al. ³⁹	Pall rings	O ₂ of the air	Water	Gas-side resistance neglected
Maćkowiak ¹¹⁵	Montz B1, C1, Gempak 2A	CO ₂ in air	Water	Gas-side resistance neglected
Benadda et al. ²⁴	Berl saddles	CO ₂ in N ₂	Water	Gas-side resistance neglected
Moucha et al. ¹²⁰	Modified Intalox saddles	O ₂ of the air	Water	Gas-side resistance neglected
Hoffmann et al. ⁸	Pall rings	NH ₃ in air (saturated with water)	Water	k_G subtracted from K_G
Kim and Deshusses ¹²¹	Lava rocks, porous ceramic beads and Raschig rings, Pall rings, polyurethane foam	O ₂ of the air	Water	Gas-side resistance neglected
San-Valero et al. ¹¹⁶	Flexiring, Refilltech, PAS Winded Media	O ₂ of the air	Water	Gas-side resistance neglected

Table 10. Main Characteristics of the Methods Using Desorption to Determine k_L

Source	Packing	Gas	Liquid
Sherwood and Holloway ⁹⁸	Raschig rings, Berl saddles, tiles	Air	CO ₂ in water O ₂ in water H ₂ in water
Molstad et al. ^{107,140}	Raschig rings, Berl saddles, spiral rings, partition rings, drip-point grids, wood grids	Air	O ₂ in water
Jones ¹⁴¹	Raschig rings	Air	CO ₂ in water
Vivian and Whitney ¹⁴²	Raschig rings	Air	O ₂ in water
Deed et al. ¹⁴³	Raschig rings	Air	CO ₂ in water O ₂ in water
Landau et al. ¹⁰⁸	Raschig rings	N ₂	UF ₆ in heavy oil
Whitney and Vivian ⁹⁹	Raschig rings	Air	O ₂ in water
Vivian and King ¹⁴⁴	Raschig rings	Air (saturated with water)	CO ₂ in water O ₂ in water H ₂ in water Propene in water
Linek et al. ³⁹	Pall rings	N ₂ (saturated with water)	O ₂ in water
Henriques de Brito et al. ¹⁴⁵	Mellapak 250.Y, 500.Y	Air	O ₂ in water
Kolev and Nakov ¹⁴⁶	Turbo-Pack	Air	CO ₂ in water
Laso et al. ³	Mellapak 125.Y, 250.Y, 500.Y	Air (saturated with water)	O ₂ in water
Brunazzi and Paglianti ¹⁴⁷	Mellapak 250.Y, Sulzer BX	Air	CO ₂ in water
Murrieta et al. ⁹⁷	Flexipac-2, Intalox 1T, Intalox 2T, Sulzer BX, Pall rings	Air	O ₂ in water
Valenz et al. ⁴	Mellapak 250.Y, 350.Y, 452.Y, 500.Y	N ₂ (saturated with water)	O ₂ in water
Wang et al. ^{5,55,56}	Mellapak 2X, 250.X, 250.Y, GT-Pak 350Y, 350Z, 500Y, A 350Y, B 350X, Raschig Hybrid 200X, 250Y, Flexipac, Raschig Super-Pak, Raschig Super-Ring, Pall rings	Air	Toluene in water
Rejl et al. ⁵⁷	Super-Pak 250.Y	N ₂ (saturated with water)	O ₂ in water
Kunze et al. ¹⁰	Pall rings, Mellapak 250.Y	Air	CO ₂ in water

Systems where $k_L a_e$ was determined by subtracting out the gas-side resistance from $K_G a_e$ or $K_L a_e$ include the absorption of NH₃ (0.2–1.29 mol%) into water,⁸ and the absorption of ketones with longer carbon chain (0.07–2.59 mol%) into water,¹⁰⁴ where $k_G a_e$ was too low to be measured simultaneously using Assumptions 1 and 2.

Cases where $k_G a_e$ and $k_L a_e$, were determined simultaneously involved the absorption of NH₃, SO₂ or ketones into water. Landau et al.¹⁰⁸ also performed the absorption of UF₆ into a heavy oil. The solutes were mixed to either air or N₂ in the concentration range of 0.12–18 mol%.

Several authors^{8,39,73,99,131,134,137,138} saturated the gas phase with the absorbent before the absorption column in order to avoid the evaporation of the liquid. The effects of evaporation were discussed in the section “Determination of the Gas-Side Mass-Transfer Coefficient—Physical absorption.”

In summary, the determination of $k_L a_e$ by physical absorption of a poorly soluble gas has been widely applied in the literature. The gas-side resistance is completely eliminated if the gas phase is pure, but due to the low solubility of the gas, it is customarily neglected even if the solute is mixed to a carrier gas. The system CO₂—water is applied in the majority of the cases: it can be easily handled and the gas phase concentration can be conveniently measured by an infrared gas analyzer. If pure CO₂ is used, care must be taken to avoid the saturation of the liquid phase. If the solubility of the gas is not low enough to neglect gas-side resistance, $k_G a_e$ can be measured separately or calculated by a correlation, however, the obtained $k_L a_e$ values will be affected by the eventual uncertainties of $k_G a_e$.

Desorption

The desorption of a poorly soluble gas can also be used to determine $k_L a_e$. As with physical absorption, the gas-side resistance can be neglected if the solubility is low enough. If the partial pressure of the solute in the gas phase is negligible then for a packed column, Eq. 9 leads to an expression for k_L that is conveniently independent of thermochemical properties:

$$k_L = \frac{L}{Ha_e} \ln \left(\frac{x_{in}}{x_{out}} \right) \quad (40)$$

Desorption is more convenient to implement⁴ with better accuracy than physical absorption.⁹⁸ With a low solubility solute the fractional gas-side concentration gradient along the column becomes small within only a short height. This leads to uncertainties in evaluating the desorption flux from gas phase measurements for long beds. The liquid phase solute concentration is therefore the preferred measurement. The maximum bed height is then only constrained by detection limit of the analytical method. Landau et al.¹⁰⁸ did not use a poorly soluble gas, but applied their method presented in the section “Determination of the Liquid-Side Mass-Transfer Coefficient—Physical absorption” to also simultaneously determine $k_G a_e$ and $k_L a_e$ by desorption. Table 10 lists the articles using desorption.

The solutes that have been used are CO₂ and O₂ in the majority of the literature sources, owing to their ease of use and analysis. H₂⁹⁸ and organic compounds with limited solubilities in water (propene and toluene) have also been used.

Table 11. Main Characteristics of the Methods Using Chemical Absorption to Determine k_L

Source	Packing	Gas	Liquid	Principle
Van Krevelen and Hoftijzer ¹²⁴	Rings, spheres	CO ₂	Caustic solution	Instantaneous reaction
Van Krevelen et al. ¹¹⁸	Rings	NH ₃ in air	H ₂ SO ₄ (aq)	Instantaneous reaction
		H ₂ S in air	NaOH (aq)	
Danckwerts and Gillham ⁶⁰	Raschig rings	Pure CO ₂ (saturated with water vapor)	K ₂ CO ₃ + KHCO ₃ + NaOCl (aq)	Danckwerts' plot and analogy with a stirred cell
			NaOH + Na ₂ SO ₄ (aq)	Analogy with a stirred cell
De Waal and Beek ¹³⁴	Raschig rings	O ₂ of the air	Na ₂ SO ₃ + Co ²⁺ (aq)	Danckwerts' plot
Jhaveri and Sharma ²⁹	Raschig rings	O ₂ of the air	CuCl + HCl (aq)	Danckwerts' plot
Onda et al. ³¹	Raschig rings	O ₂ of the air, in air, or in pure form	Na ₂ SO ₃ + CoSO ₄	Danckwerts' plot
Joosten and Danckwerts ²²	Raschig rings, Intalox saddles	Pure CO ₂	KHCO ₃ + K ₂ CO ₃ + KAsO ₂ (aq)	Danckwerts' plot
			K ₂ HPO ₄ + KH ₂ PO ₄ (aq)	Slow reaction
			NaOH + NaNO ₃ + sugar (aq)	Instantaneous reaction
Rizzuti et al. ^{37,61} , Rizzuti and Brucato ⁶²	Raschig rings	Pure CO ₂	K ₂ CO ₃ + KHCO ₃ + KAsO ₂ - sugar (aq)	Danckwerts' plot
Weiland et al. ⁴⁰	Montz A2, Goodloe	CO ₂ in air	Na ₂ CO ₃ + NaHCO ₃ (aq)	Slow reaction
Benadda et al. ⁴²	Raschig rings	CO ₂ in air	Na ₂ CO ₃ + NaHCO ₃ + NaOCl (aq)	Danckwerts' plot
Roesler et al. ¹⁴⁸	Mellapak 250.X, 250.Y, IFPACC™ 2X	CO ₂ in air	MDEA + CO ₂ (aq)	Slow reaction

Laso et al.³ have warned that the solubility of CO₂ is rather high compared to that of O₂, for example, and that the cations present in water (unless deionized) might affect the results. The liquid phase has been water in all sources, and the gas phase air or, in one case N₂.⁴ Vivian and King,¹⁴⁴ Linek et al.,³⁹ Laso et al.,³ Valenz et al.,⁴ and Rejl et al.⁵⁷ humidified the gas phase before the desorption column to minimize liquid interfacial temperature gradients from evaporation. Kunze et al.¹⁰ achieved saturation of the gas phase by recirculating it.

The saturation of the water with the solute was realized in different ways. Several authors^{97,99,146} introduced the gas into the water stream before the column from a gas cylinder, some^{3,39,147} saturated the water in a tank before the experiments, while others used an absorption column.^{143,144} Wang et al.⁵⁵ simply mixed toluene and water in a tank at the start of the experiment since their solute is a liquid at room temperature, and then continuously added a toluene make-up into the tank, because their liquid phase was recirculated.

In summary, the desorption of a poorly soluble gas, typically CO₂ or O₂ into water, is a convenient and popular method to determine $k_L a_c$. The use of O₂ is likely to yield more precise results. The gas-side resistance is never completely eliminated, but the low solubility makes it negligible. Chemical analysis, usually that of the liquid phase, is necessary, but for the gases mentioned above, the analysis methods are well established.

Chemical absorption

The liquid-side mass-transfer coefficient can also be determined by methods using chemical absorption. The reactions applied belong to three different reaction regimes: they can be instantaneous (or very fast), of intermediate speed, or slow. The resistance of the gas phase has to be negligible, which is often the case with the systems and conditions used. An overview of these methods is given by Sharma and Danckwerts¹² and Laurent et al.¹³ Danckwerts and Gillham⁶⁰ used a particular approach using the analogy of the packed column to a stirred cell. The methods found in the literature are listed in Table 11, where the principle of the determination of $k_L a_c$ is also given.

Instantaneous or Very Fast Reactions. A reaction can be considered instantaneous if:

$$Ha \gg E_{inf} \quad (41)$$

Sharma and Danckwerts¹² give this condition:

$$Ha > 10E_{inf} \quad (42)$$

In practice, the constraint can be relaxed to $E_{inf} > 4$.¹³ This is the same reaction regime as the one used for the determination of $k_G a_c$, but here the condition on k_G is inverted:

$$k_G p \gg k_L B^0 \quad (43)$$

This means that the gas-side resistance is negligible, and the reaction does not take place on the gas-liquid interface.

When the following additional criterion:

$$\frac{D_B B^0}{D_A v A^*} \gg 1 \quad (44)$$

is also met, meaning that the liquid phase reagent is in great excess compared to the equilibrium concentration of the solute in the liquid phase without reaction, then the enhancement factor becomes:

$$E \approx E_{inf} = \frac{D_B B^0}{D_A v A^*} \quad (45)$$

This ensures that the solute concentration is virtually zero in the bulk liquid ($A^0 = 0$). By substitution, the volumetric mass transfer rate becomes independent of the concentrations A^0 and A^* :

$$\Phi = E k_L a_c (A^* - A^0) = \frac{D_B B^0}{D_A v} k_L a_c \quad (46)$$

and $k_L a$ can be calculated merely by measuring B^0 . An advantage of this method is that it is not necessary to know the solubility of A . In essence, what is happening is that the limiting factor is the diffusion of the reagent to the reaction zone near the interface within the liquid film and not the reaction rate, therefore the flux is controlled by only physical terms.

Reactions that can be used (Table 11) include the absorption of NH_3 into sulfuric acid, of SO_2 , Cl_2 , or HCl into alkalis, of H_2S or HCl in solutions of amines. Under certain conditions, the absorption of O_2 from air into dithionite solution, or that of pure CO_2 into amine solutions can also be appropriate.¹² Van Krevelen and Hofstijzer¹²⁴ and Joosten and Danckwerts²² used the absorption of CO_2 into caustic solutions.

Danckwerts' Plot (Intermediate Reaction Regime). If the reaction is in the intermediate reaction regime, ($\text{Ha} \ll E_{\text{inf}}$ and $E < 9$ according to Sharma and Danckwerts¹²) the Danckwerts' plot can be used to simultaneously determine k_L and a_e . The method was described in detail in the section "Determination of the Effective Interfacial Area—Chemical absorption—Danckwerts' plot (intermediate reaction regime)." The uncertainty of k_L is higher than that of a_e , as it is determined from the intercept of the plot $\Phi^2 - kB^0$, while a_e is calculated from the slope. If the gas-side resistance is not negligible, it can also be taken into account.

Reaction systems used have been the absorption of CO_2 into sodium or potassium bicarbonate buffer solutions, with either NaOCl or KAsO_2 as catalyst (Table 11). The Danckwerts' plot was created by varying the concentration of the catalyst. Under certain conditions, the reaction of O_2 and CuCl can belong to this regime.²⁹ Some authors absorbed O_2 into solutions of sodium sulfite with Co^{2+} ions as catalyst.

When the solute was CO_2 , most authors used it in pure form, except Benadda et al.⁴² where the CO_2 concentration was 10% in air. The authors estimated the gas-side resistance to be negligible. The absorption of O_2 was performed by using air, except for Onda et al.³¹ who ran experiments over the entire concentration range from air to pure O_2 . The gas phase was humidified by air before the absorption in some cases^{60,134} in order to reduce evaporation and avoid cooling of the liquid phase.

Slow Reactions. In the slow reaction regime, the rate of solute reaction in the liquid film is small to the extent that concentration of the solute can be considered constant in the film, and thus $E \approx 1$. The criterion for this condition is that:

$$\text{Ha} < 1 \quad (47)$$

as specified by Laurent et al.,¹³ or:

$$\text{Ha}^2 \ll 1 \quad (48)$$

according to Sharma and Danckwerts.¹²

The reaction must simultaneously be fast enough to keep the solute concentration negligibly small in the bulk liquid. The following inequality must then be satisfied:

$$k_L a_e \ll l k B^0 \quad (49)$$

where l is the volume of liquid phase per unit volume of packing. When these conditions are met, the volumetric mass transfer rate is equal to that of physical absorption:

$$\Phi = k_L a_e A^* \quad (50)$$

therefore, $k_L a_e$ can be calculated by measuring the absorption rate, and by knowledge of A^* . If the concentration of A in the bulk gas is approximately constant, then A^* is also constant, and can be easily calculated; otherwise, the variation of A in the column must be estimated. Advantageously, neither the kinetics, nor B^0 for that matter need to be known with great precision as they do not appear in the mass transfer rate expression. Note that gas-side resistance was neglected here.

If the reaction is not fast enough to consume all the solute in the bulk liquid, the following approach can be used. The measured reactive volumetric mass-transfer coefficient $k_{L,R}$ is:

$$\frac{1}{k_{L,R} a_e} = \frac{1}{k_L a_e} + \frac{1}{l k B^0} \quad (51)$$

By varying either k (through catalyst concentration), or B^0 , and plotting $1/k_{L,R} a_e$ against $k B^0$ as a straight line, $k_L a_e$ can be obtained from the intercept.

According to Sharma and Danckwerts,¹² suitable chemical systems are the absorption of CO_2 into carbonate-bicarbonate buffer solution without catalyst, or that of O_2 into dilute acid solutions of CuCl , or into Na_2SO_3 solution using CoSO_4 or CuSO_4 as catalyst. For packed columns, the absorption of CO_2 into bicarbonate and phosphate buffer solutions were used (Table 11). Recently, Roesler et al.¹⁴⁸ used a system based on the absorption of low partial pressures of CO_2 (1.5 kPa or less) into a partially loaded solution of dilute methyl diethanolamine (MDEA) solutions (3% wt) to determine the $k_L a$ of various structured packings. These reactants provided an irreversible pseudo-first order reaction system in the slow regime for loadings between 0.1 and 0.2 mol- CO_2 /mol-MDEA. The rather weak absorption fluxes and consequently slow depletion rates of the gas phase solute make this method well suited for columns with NTU_L greater than 2 where physical desorption methods may lead to high uncertainties.

Analogy Between a Packed Column and a Stirred Cell. This method was used by Danckwerts and Gillham,⁶⁰ and is described in the section "Determination of the Effective Interfacial Area—Chemical absorption—Other methods." The main idea is that if the enhancement factors in a stirred cell and in a packed column are equal for the same chemical system and compositions, then the k_L values are also equal. CO_2 is absorbed into inert and reactive solutions such as those of bicarbonate buffer and NaOH in water. For any stirring speed of the cell, there exists a liquid flow rate of the packed column at which the enhancement factors of both systems are equal. At this point, the k_L measured in the stirred cell is equal to that of the column. Since the interfacial area of the stirred cell is known, it is possible to measure k_L instead of $k_L a_e$.

Conclusion on Chemical Absorption Methods. The chemical absorption methods use a variety of reaction systems, belonging to three reaction regimes, to determine the liquid-side mass-transfer coefficient and usually involving the absorption of CO_2 and O_2 . The intermediate regime is the one most frequently applied, whereby the method of the Danckwerts' plot is used, although k_L is likely to be more uncertain, since it is calculated from the intercept of the plot. Bicarbonate buffer solutions with different catalysts have been applied by several authors. Whatever the regime, the test conditions must be carefully checked to satisfy the required criteria, as their validity may change from run to run and even along the column, depending on the concentration of the reagents.

Tomography

A novel method proposed by Schug and Arlt¹⁴⁹ aims to determine k_L by computer tomography using x-rays. The idea is to measure the concentration of the solute directly in the liquid phase, by relating the greyscale values of the pixels (resolution: $80.52 \mu\text{m} \times 80.52 \mu\text{m}$) in the liquid phase to the local solute concentration. The solute must have high molecular weight to absorb x-rays sufficiently, and must be soluble enough to reach sufficient concentrations for identification.

Dichloromethane was identified as a good solute candidate. The authors stated that the liquid film on the packing is thick enough (at least 10 pixels) to enable the application of the method if the viscosity is higher than 2 mPa-s, and they recommend absorption into isopropanol or other alcohols with longer carbon chains. The tests were performed in a 5 cm diameter column filled with 20 cm of an unspecified Mellapak packing. At the time of the completion of this manuscript, no further test results have been published.

Conclusions

The methods for determining liquid-side mass-transfer coefficients belong to two main groups: physical absorption or desorption of a poorly soluble gas and chemical absorption. With a solute of very low solubility the liquid-side mass transfer resistance becomes dominant while that of the gas-side can be neglected. If the gas phase is purely the solute, then the gas-side resistance is completely eliminated, at the risk however of rapidly saturating the liquid phase. If the gas-side resistance is not negligible, it is possible to determine both $k_G a_e$ and $k_L a_e$ based on assumptions on their dependence to gas and liquid flow rates, but this method is not recommended, as it likely introduces additional errors.

Physical absorption or desorption of CO_2 and O_2 into water are the most popular methods as these solutes have very low solubility and have well established analytical methods. In the case of physical absorption, the useful bed height is more limited due to saturation and uncertainties on the equilibrium value, whereas with desorption the measurement error is only determined by the precision of the analysis.

Chemical absorption, although less common than the above methods, has been used with various reaction systems covering the different regimes. Systems in the instantaneous and slow regimes seem to yield more precise results than those in the intermediate regime, which involves using Danckwerts' plots to determine a_e from the slope and k_L , with rather large uncertainties, from the intercept. The magnitude of the gas-side resistance must be checked, as it is not always negligible, and the validity of the applied reaction regime must be verified, which requires some knowledge of the kinetics.

More recently, x-ray tomography has also been proposed to measure local solute concentrations in the liquid phase and determine k_L , but results are not available at this time.

The choice of the most appropriate method to determine k_L depends on the packing characteristics, bed geometry and fluids available. When the packed bed NTU_L is low (small bed heights or low $k_L a$) we recommend desorption as it does not call for the use of thermochemical parameters if the solubility is low. Preferred systems are oxygen from water into N_2 if the latter is available in sufficient quantity, otherwise CO_2 from water into air or N_2 , or toluene from water into air although this solute has toxicity issues. When the bed NTU_L is large (tall beds and large $k_L a$), then the solute depletion in the liquid phase can become excessive and lead to high measurement uncertainties. In such cases, the chemical absorption of CO_2 added to air into MDEA solutions may offer a reliable method provided the thermochemical parameters are well established.

Treatment of Internal and External End Effects

The aim of the methods presented above is to determine the mass transfer parameters of packing under fully developed flow conditions. However, depending on how the column is configured, three secondary sources of mass transfer can be

identified that distort the measurement. One takes place in the regions between the packing ends and the gas/liquid sampling positions for chemical analysis and is referred to as the external end effects, the values of which depend on the column configuration, distributor performance and the type of packing. A second takes place in the free ends of the packed bed or of the packed element where the gas (at the bottom) and the liquid (at the top) flow regimes are not yet well established. These regions will change the packing efficiencies, generally in an adverse manner, and are referred to as the internal or entrance (end) effect.¹⁵⁰ Their impact will depend on the performance of the distributor as well as on the self-distribution capability and channeling tendency of the packing. The external and internal end effects are almost always treated together under the name "end effects." Their magnitude depends on the gas and liquid flow rates⁷¹ and, depending on the situation, may vary from only a few percent to more than half of the total absorption.¹¹¹ Several authors neglect end effects, by simply stating that they are minimized by the column configuration and distributors used. In view of the potentially high impact of end effects, it is strongly recommended to evaluate them.

The third source of secondary mass transfer is generated by the liquid film along the walls of the column, the contribution of which will decrease with diameter roughly as $1/D_c$. Vidwans and Sharma²⁸ recommend for random packings that the column diameter should be at least eight times the packing size in order to obtain representative values of a_e . Fair¹⁵¹ states that wall effects become negligible for diameters larger than 0.6 m.

There is some evidence that the magnitude of end effects also depends on the chemical system, for example, Yoshida and Koyanagi⁷¹ measured higher end effects for vaporization than for physical absorption. The difference decreased with increasing L , and above certain liquid flow rates, end effects became constant. Higher end effects for vaporization might be explained by a difference in the effective interfacial area of the liquid outside the packed bed.

Experimentally, the end effects can be quantified by either taking samples at different locations of the column, or by performing measurements with multiple packed bed heights. With samples immediately below and above the packings (e.g., Molstad et al.¹⁰⁷; Vivian and Whitney⁹⁹; Houston and Walker¹¹¹; Weiland et al.⁴⁰; Kolev et al.¹⁹; Kunze et al.¹⁰), the mass transfer taking place outside of the column can be measured. However, the internal effects are not eliminated. To overcome this problem, samples can be taken within the packing^{4,9,39,54,57,120,152} as well. This procedure assumes that the sampling system inside the packing does not significantly perturb the flow and hence the mass transfer rates in the packing.

Repeating experiments with at least two different packing heights is easier to realize, but the applicable height can be limited for certain measurement methods, such as vaporization of a pure liquid. Instead of actually changing the height of the bed, some authors (e.g., Danckwerts and Gillham⁶⁰; Alper³⁵) vary packing height by allowing the bottom of the column to fill up with liquid at different, controlled heights. The location of the gas inlet is varied accordingly, so as to be immediately above the liquid seal. The surface of the liquid, however contributes to the end effects.

The end effects are sometimes regarded as a virtual layer of packing with an equivalent packed bed height (H_E). This approach is not theoretically sound, as the dependency of H_E

on G and L might not be the same as for the packing.^{71,93} The equivalent bed height can be determined by trial and error^{91,93}: it is the extra packed bed height that has to be added to the physical one to bring the results of different bed heights into agreement.

The calculation of the true mass-transfer coefficient, when different packing heights are used, is based on the following equation:

$$NTU'_{OG} = NTU_{OG} + NTU_E \quad (52)$$

where the prime sign denotes the NTU measured, the unmarked NTU is that of the packing without the end effects, and NTU_E is the end effects. If experiments are performed for two heights H_2 and H_1 , the true NTU is obtained for the packing height $H_2 - H_1$ as⁶⁵:

$$(NTU_{OG})_{2-1} = \frac{H_2 - H_1}{HTU_{OG}} = (NTU'_{OG})_2 - (NTU'_{OG})_1 \quad (53)$$

An alternative equation to calculate the true HTU from the measured HTU values was given by Lynch and Wilke⁸⁷:

$$HTU_{OG} = \frac{(HTU'_{OG})_2 (HTU'_{OG})_1 (H_2 - H_1)}{H_2 (HTU'_{OG})_1 - H_1 (HTU'_{OG})_2} \quad (54)$$

The end effects NTU_E can be calculated as the difference of the measured and the true NTU of the same packed bed height, or directly with the following equation⁷¹:

$$NTU_E = \frac{H_1 (NTU'_{OG})_2 - H_2 (NTU'_{OG})_1}{H_1 - H_2} \quad (55)$$

If more than two heights were used, they can simultaneously be taken into account by plotting the measured $(K_G a_e)'$ vs. $1/H$.^{86,90,112} By transforming the basic equation, we can obtain:

$$(K_G a_e)' = K_G a_e + NTU_E G \frac{1}{H} \quad (56)$$

A straight line fitted on the measurement points intercepts the ordinate at the true value of the mass-transfer coefficient, while NTU_E can be calculated from the slope of the line. H_E can be obtained as the distance between the origin and the intercept of the fitted line with the abscissa.^{90,112} For two packing heights, this method gives the same results as the ones presented earlier. All of these methods assume that the true HTU is independent of the height of the packed bed, that is, all the variation of HTU with H is due to the existence of additive end effects.

The existence of internal effects, however, means that efficiency is not constant in the inlet zones of the packing; therefore, the change of NTU with the packed bed height is not linear for low H values (Figure 6¹⁵⁰). If NTU is measured at two heights H_1 and H_2 at the linear part of the curve, the previously presented methods can be used to determine the end effects NTU_E that is the sum of the external end effect NTU_{EE} (NTU measured without packing) and the internal end effect NTU_{IE} . However, if measurements are performed at the non-linear part of the curve, the end effects will be underestimated, and the mass-transfer coefficient overestimated.

Among other approaches to treat end effects, Nakov and Kolev¹¹⁹ placed a liquid redistributing bed above the packing to be measured. They assumed the end effects to be equal to the mass transfer measured only in the presence of the redistributing layer. In this way, only the external effects are corrected, but the absorption in the redistributing layer is likely to

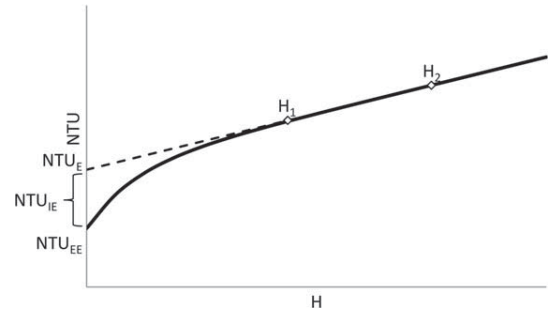


Figure 6. The change of NTU with the height of the packed bed; the internal (NTU_{IE}) and external (NTU_{EE}) effects (based on Billet¹⁵⁰).

be much higher than the internal effects. Wang et al.⁵ measured the mass transfer rates in the column sections below and above the packing, and expressed these (external) end effects as NTU_E . They found that wall and end effects could be more important for coarser structured packings. Others have estimated end effects not by measurements but by calculation. For instance, Tsai¹⁵³ took end and wall effects into account for the determination of a_e by subtracting their contribution to a_e from the measured value. The a_e attributed to the column sections below and above the packing was calculated on the basis of the work of Yeh,¹⁵⁴ by treating these sections as spray columns with spray impacting a solid surface (above the packing), or into a liquid (below the packing). The contribution of the wall to a_e was calculated by assuming complete wetting. Roesler and Raynal⁶³ and Alix and Raynal¹⁵⁵ took the wall effect into account by using the a_e/a'_g ratio, instead of simply a_e , where a'_g contains the specific superficial area of the column wall, as well:

$$a'_g = (a_g)_{\text{packing}} + \frac{4}{D_c} \quad (57)$$

This approach assumes that the wettability of the packing and the wall is identical. In fact, it is implicitly assumed that the same fraction of the geometrical surface is effective.

In conclusion, while end effects can be reduced by choosing an appropriate column configuration, it is nonetheless recommended that they be assessed as they can significantly contribute to the overall mass flux. Experimentally this can be performed by taking fluid samples immediately after the packing inlet and exit planes, or even within the packing, in addition to taking fluid samples at the inlet and outlet of the column. Alternatively, at least two different packed bed heights can be used.

Influence of Packed Bed Height

It is often assumed that the intrinsic mass transfer parameters are independent of the packed bed height, and that measured variations are due entirely to the end effects. The literature is, however, contradictory on this issue with some studies finding a dependency of these intrinsic mass transfer parameters to bed height^{41,73,89,110,124,129,138,147,156} and others not reporting any.^{30,60,98} The evolutions along the bed most likely originate from flow pattern changes particularly for the liquid. The initial flow pattern will depend on the type and position of the liquid distributor. Further along the bed, the ratio of the packing size and column diameter (D_c/D_p), the ratio of the bed height and column diameter (H/D_c), the

packing type, hydraulic loads and liquid properties will affect the liquid flow distribution. This section describes the phenomena affecting the liquid flow and the impact on mass transfer parameters.

Evolutions of the liquid flow distributions along packed beds

The liquid entering the packed bed has an initial distribution, whose quality is determined by the liquid distributor. A good initial distribution (which is usually, but not always a uniform one¹³⁸) neither leaving a large part of the packing dry, nor leading to excessive wall flow, is important for proper functioning of the column.

The liquid flowing down the packed bed will establish a stabilized distribution pattern only after a certain distance from the liquid distributor (1–2 packing layers for structured packings), and thus there exists a minimum packed bed height necessary to measure height-independent mass transfer parameters. Maćkowiak and Maćkowiak¹⁶ recommend a H/D_c ratio higher than 2.5, and a bed height exceeding 1 m.

The quality of liquid distribution can deteriorate with increasing bed height. This maldistribution phenomenon is defined as a deviation of the real flow pattern from the plug flow used in most column models. Maldistribution may be generated at the inlet due to the distributor or throughout the bed owing to the nature of the packing. Excessively long packed beds should therefore not be used: in industrial columns liquid redistribution generally becomes necessary after 2–3 m height (15–20 theoretical stages), although well-functioning columns with packed beds higher than 10 m packing exist.¹⁵⁷ Maldistribution can manifest itself in axial mixing, in incomplete wetting of some parts of the packing, and in the tendency of the liquid to spread toward the wall of the column, and once reaching it, to flow along the wall. Wall flow is undesirable, as it reduces the effective interfacial area of the column, and changes the local L/G ratio, although k_G and k_L may increase through intensive mixing where the packing elements touch the wall.¹³⁸ A high D_c/D_p ratio helps to avoid excessive wall flow. The following values are recommended (see also the section “Standardization”): $D_c/D_p \geq 10$ for random packings,⁸ $D_c \geq 200$ mm for structured packings.¹⁵⁸ For random packings, liquid spreading is rather limited particularly with smaller D_p . In the case of structured packings, however, the ordered structure allows radial spreading of the liquid. Wall wipers, on the other hand, reduce wall flow by redirecting the liquid toward the packing. Denser packings (such as random packings) may be less sensitive to the increase of H .⁴¹ For more information on maldistribution, the reader is referred to the book of Górak and Olujić.¹⁵⁹ Brunazzi and Paglianti¹⁴⁷ pointed out that the effect of the packed bed height cannot be solely attributed to liquid maldistribution if mixing in the contact points between packing elements is incomplete.

Mass transfer parameter evolutions with bed height

The experimental results indicating an influence of packed bed height will be discussed in the following sections. Results on the effect of column diameter are also included. With two exceptions,^{41,148} all the experiments were performed with random packings. In all the cases, if a dependency was observed, the mass transfer parameters decrease with increasing packed bed height, and increase with increasing column diameter.

Effective Interfacial Area. The evidence of the effect of H on the interfacial area is scant. Yoshida and Koyanagi⁷³ performed experiments with two packed bed heights, and found that a_e was higher for the shorter packed bed. This could be explained by different magnitudes of end effects and/or by worse liquid distribution in the higher bed. Based on the experimental work available in the literature on the determination of a_e by chemical absorption, Charpentier¹⁴ concluded that in the trickle flow regime a_e is independent of H , but increases with D_c . Henriques de Brito et al.⁴¹ found with Mellapak 125.Y that a_e is reduced by increasing H . The magnitude of reduction, however, depends on L , and is greater for low liquid loads. The authors explain this by a stronger influence of channeling effects at lower flow rates. Based on distillation results, Bravo and Fair⁶⁷ proposed a correlation in which a_e is proportional to $H^{-0.4}$ for random packings. From the above literature the effect of bed height, if any, is generally to degrade the effective area.

Gas-Side Mass-Transfer Coefficient. Studies dealing with the dependency of the gas-side mass transfer parameter on H are also scarce. Van Krevelen et al.⁸⁹ found that k_G is proportional to $(D_c/H)^{1/3}$. Molstad and Parsly¹¹⁰ concluded on the basis of previous measurements that unlike $k_L a_e$, $k_G a_e$ is dependent on H , being approximately proportional to $H^{-1/3}$.

Correlations found in the literature generally do not take the packed bed height into account. Exceptions include the correlation of Wagner et al.,¹⁶⁰ developed for distillation with random packings, which gives k_G as proportional to $H^{-0.5}$, and those of Piché et al.,^{161,162} which were obtained with the use of artificial neural networks based on an extensive database of absorption measurement results.

Liquid-Side Mass-Transfer Coefficient. More extensive research on the effects of bed height has been conducted concerning the liquid-side mass-transfer coefficient. Van Krevelen and Hoftijzer¹²⁴ found that k_L is proportional to $(D_c/H)^{1/3}$, just as for k_G . According to Fujita et al.,¹⁵⁶ $k_L a_e$ is proportional to $H^{-0.19}$. Yoshida and Koyanagi⁷³ observed an increase in HTU_L with H that they considered too high to be explained only by the existence of end-effects, and they supposed that $k_L a_e$ decreases with increasing H . Cornell et al.¹⁶³ suggested an exponent of -0.15 based on the evaluation of experimental results of several authors. However, as results from different sources are used, this value might have a significant error. An effect of D_c was not observed.

The aim of Hikita et al.¹³⁰ was to clarify whether H has an effect on HTU_L or not. The authors performed experiments with two columns (diameters: 6.6 and 12.5 cm) using Raschig rings with bed heights between 0.05 and 1.50 m. They found that H had no effect in the larger diameter column. In the case of the smaller column, the authors classified three regions (A, B, and C) on a map of H vs. L . Region A was for high flow rates, Region B for low flow rates with short beds or medium flow rates with higher beds, while Region C was for low flow rates and high beds. The packed bed height had no effect in Region A, while HTU_L was proportional to $H^{0.08}$ in Region B and with $H^{0.44}$ in Region C. The effect of H is explained by the authors as the result of the potential non-uniformity of the liquid distribution.

Mangers and Ponter¹³⁸ found that $k_L a_e$ decreased with increasing H (varied between 25 and 75 cm) both for readily and poorly wettable ring packings. They also measured the ratio of wall flow to total flow as a function of H , and the

increase of wall flow with H can be an explanation of the diminishing $k_L a_e$.

Brunazzi and Paglianti¹⁴⁷ state that increasing H decreases k_L if mixing at the contact points between packing elements (called junctions by the authors) is incomplete, both in the case of random and structured packings. As shown experimentally and theoretically by Nawrocki and Chuang¹⁶⁴ for absorption into stable rivulets on an inclined plate, the flow distance of the liquid influences considerably the mass transfer. In the case of complete mixing, the flow distance is a function of geometry of packing elements, for example, that of channel dimensions for structured packings. If partial mixing occurs, the flow distance is the distance covered by the liquid from the top to the bottom of the column, which is certainly related not only to packing dimensions, but to the packed bed height, as well. The effect of H was observed only at $H > 1$ m, and below a critical Re_L value (100). The column diameter was 10 cm; the packings used were Sulzer BX and Mellapak 250.Y. Note that these findings are in accordance with results of Hikita et al.,¹³⁰ and suggest that not only the packed bed height, but also the liquid flow rate is important.

As in the case of k_G , correlations generally do not contain H as a parameter. Exceptions are the correlation of Wagner et al.¹⁶⁰ in which k_L is proportional to $H^{-0.5}$ for random packings, that of Brunazzi and Paglianti,¹⁴⁷ and those of Piché et al.^{161,162} obtained with the use of artificial neural networks.

Standardization

As pointed out in the introduction of the article, the often strong variation of experimental data on mass-transfer coefficient obtained from different sources with the same packing calls for the standardization of the measurement methods. More reliable and comparable mass transfer parameters could lead to a reduction of safety factors in column design, and thus a reduction of investment and operating costs.¹⁰ However, unlike for distillation, no standard has been established for absorption.

Hoffmann et al.⁸ recommended the use of the following chemical systems: absorption of low concentration CO_2 in aqueous NaOH solutions for a_e , absorption of SO_2 into NaOH solutions for k_G , absorption of NH_3 in water for k_L . The desorption of CO_2 from water is mentioned as an alternative to measure k_L , but it was not applied by the authors. Both by the determination of a_e and k_L , the gas-side resistance was taken into account by subtracting its value, calculated on the basis of the SO_2 absorption measurements, from the overall resistance. The relative error was the highest in the case of a_e , as it reached values of 30%. This error propagated to k_G and k_L as well through the division of $k_G a_e$ and $k_L a_e$ by a_e .

Hoffmann et al.⁸ state that the physical properties must have high accuracy in order to reduce the error of the evaluation. They have selected a set of properties from the literature deemed to be most accurate for the systems used. Concerning the experimental setup, they have defined the following set of requirements:

- Isothermal experiments to avoid variations of system properties. This can be achieved by performing experiments at room temperature, using heating jacket and tempering the feed streams.
- Minimization of wall effects to ensure reliable scale-up data. For structured packings D_c should be higher than 20 cm (as recommended by Olujić¹⁵⁸) for random packings the ratio D_c/D_p should be higher than 10.

- Minimization of evaporation by pre-saturation of the gas flow in order to ensure single component mass transfer.

- Uniform initial gas and liquid distribution to avoid maldistribution and inlet effects by installing suitable and technical relevant gas and liquid distributors (>100 – 200 drip points/ m^2 for industrial scale).

- Consideration of absorption in the bottom of the column to account for end effects at the bottom of the column by measuring fluid compositions both at the column bottom inlet/exit and directly below the packing.

- Measurable outlet gas composition (in the case of absorption) to ensure mass transfer along the complete column height, that is, avoiding the depletion of the solute in the gas phase. This can be achieved by adjusting the packing height or by using sufficiently high solute concentration in the inlet gas.

- Use of one uniform packing height for comparison with different test systems to eliminate the effects of packing height differences.

- Standardized filling method to avoid maldistribution and undefined packing structure. In order to be able to compare results, the structure of the packed bed should not show significant variation between different measurements. The average void fraction of the bed describes the packing density. However, local variations of the structure, and thus the void fraction, can induce maldistribution, and thus change the results of mass transfer measurements even if the average packing densities are identical. Measuring the dry pressure drop of the bed gives information on the structure of the bed. Measurement of the concentration profile along the column height^{165–167} can help identifying local variations in the structure of the bed.

- Representative gas and liquid samples. The composition can vary over the column cross-section. By determining gas and liquid profiles over the column cross-section, a uniform distribution can be ensured. Measurement of composition in the inlet and outlet tubes is also recommended.

Hoffmann et al.⁸ also recommend that when publishing new mass transfer correlations, researchers give the following information, as well:

- Fluid systems along with their physical and chemical properties,
- Experimental setup (D_c , H , packing geometry),
- Experimental procedure, number of data points, range of gas, and liquid loads,
- Processing method, analytical techniques, and uncertainties,
- Validity range of the proposed correlation (physical properties and loading conditions).

Rejl et al.⁹ performed an assessment of the recommendations of Hoffmann et al.⁸ They recommend the use of systems where the mass transfer resistance is only present in one phase. In view of this, $k_L a_e$ was proposed to be measured using the absorption or desorption of CO_2 or O_2 in/from water, instead of the absorption of NH_3 , where as much as 50% might lie in the gas phase. Moreover, Hoffmann et al.⁸ calculated k_L with the assumption that interfacial area measured by the absorption of CO_2 (chemical absorption) is equal to that of the absorption of NH_3 (physical absorption). For the determination of k_G and a_e , Rejl et al.⁹ recommend the same systems as Hoffmann et al.⁸ In the case of a_e , a gas velocity higher than 0.5 m/s and a OH^- concentration less than 1 mol/L are recommended, in order to make the gas-side resistance negligible.

The physical properties used should be the same as those used originally in the evaluation of the kinetic constant. The end-effects should be eliminated by taking samples directly from the packing. In the case of absorption, low outlet gas-phase solute concentrations may introduce significant error in the mass transfer parameters. To prevent this from happening, the packed height should be limited such that the gaseous solute is not depleted beyond 95% of its entrance level. The authors also investigated the effect of axial dispersion using 25 mm metal Pall rings and found that, when it is taken into account, $k_G a_e$ values are 10–15% higher while $k_L a_e$ can be up to 30% higher at low liquid loads. These dispersion effects are comparable in magnitude to the scatter among literature data for a given packing. Rejl et al.⁹ also point out that the disparity in k_L and k_G values is significantly lower for measurements performed in a given laboratory, than in different ones, which hints at the possible benefits of using a set of standardized methods to determine the mass-transfer coefficients.

The review of Schultes¹⁶⁸ on mass transfer columns research also identified the definition of test facility setup standards as one of the future research tasks. As demonstrated by measurement results from the literature, the performance of column internals depend significantly on the experimental setup and on the institute where the work has been done. The different correlations often give different results, as well. The gas- and liquid-side mass-transfer coefficients are expected to have $\pm 10\%$ deviation between measured data and values predicted with state-of-the-art correlations (e.g. Billet and Schultes¹⁶⁹) if measurements were performed on the same column with a specific packing. If multiple data sets (absorption, desorption, rectification) are used to calculate the mass-transfer coefficients, $\pm 20\%$ mean deviation can be expected. In the case of extrapolation for different physical properties or flow rates, deviations can be around $\pm 50\%$. The value of a_e is even less accurate, with $\pm 80\%$ mean deviation for interpolation and more than $\pm 100\%$ for extrapolation.

Maćkowiak and Maćkowiak¹⁶ give the following recommendations on the experimental setup. The column diameter should be high enough so that $D_c/D_p > 10$. Either the packed bed height should be higher than 1.0 m, or the ratio H/D_c should be higher than 2.5 to minimize maldistribution.

Wolf et al.¹⁷⁰ investigated the effect of experimental setup on the mass transfer measurements. Multiple sampling locations were studied both for the gas and the liquid phase. The authors recommended taking integral samples over the whole cross section of the column immediately above and below the packing. They also reported that HTU_{OG} and HTU_{OL} depend on the solute concentration. These authors called for a detailed pre-treatment procedure to ensure comparability of the results, specifically with plastic packings as their wettability increases with time until reaching a stable value. Their results showed stabilization after four cycles of irrigation and absorption (4 h of total time). Billet and Maćkowiak¹³⁹ reported that the packing efficiency and pressure drop became constant after one week of operation. Maćkowiak and Maćkowiak¹⁶ also recommended the pre-treatment of plastic packings.

Kunze et al.¹⁷¹ outlined a collaborative project with two academic and several industrial partners, including packing vendors and end users with the aim of developing standards for mass transfer measurements in absorption and desorption, for both experimental apparatus and evaluation methods. In view of rate-based simulation results, the effect of

experimental configuration, and that of the possible measurement errors are also to be evaluated. Similarly to Hoffmann et al.,⁸ the authors propose the pre-saturating the gas phase with water in a saturator column. As for the chemical systems they repeat the recommendations of Rejl et al.⁹ with the addition of the absorption of NH_3 in aqueous H_2SO_4 (also an instantaneous reaction) for k_G . For the determination of k_L , they recommended using desorption of CO_2 or O_2 from water, while Rejl et al.⁹ considered absorption, as well. These systems satisfy the criteria for the location of mass transfer resistance required for evaluating the associated mass transfer parameter. In selecting the systems, other criteria must be taken into account as well, such as ease of analysis, accuracy of physical properties, environmental and safety risks, availability, and price. The physical properties have to be calculated in a standardized way, as well.

As a result of the above project, Kunze et al.¹⁰ proposed a standardized measurement procedure and mass transfer parameter determination. The systemic, step-wise determination of the parameters was described, using three chemical systems to determine k_G , k_L , and a_e . The recommendations of Kunze et al.¹⁷¹ were reasserted, with the addition of a positive viewpoint on the use of toluene desorption from water into air, as an alternative to measure $k_L a_e$. To take into account the gas-side resistance on the determination of a_e , three possibilities were mentioned: (1) to neglect the resistance, (2) to calculate k_G from published correlations, (3) to calculate k_G from $k_G a_e$ measured by the same researchers. The first possibility could be useful to quickly compare a_e of different packings. The second option is especially interesting if the correlation was determined by the standardized methods, or by another method that is transparent and comprehensible. Otherwise, the third option is suggested, that is, using data from the same source. For test systems, calculation methods for the determination of physical and chemical properties were recommended. A sensitivity analysis highlighted that the measured concentrations and volumetric flow rates have the highest influence on the accuracy of mass-transfer coefficients, while the influence of pressures and temperatures is lower.

Kunze et al.¹⁰ also presented a case study of the proposed method, including the experimental setup, process measurements and samplings. Gas and liquid samples were taken directly below and above the packing, however, end effects were not discussed. Instead of using a pre-saturator column, the gas phase was recirculated in order to ensure its saturation with water vapor. The experimental details can be found in the project report, which is also accompanied by a software with which measurement can be evaluated.¹⁷²

As presented in this section, the issue of standardizing mass transfer measurements in absorption has been treated by multiple authors in recent years. The proposition of Kunze et al.¹⁰ is particularly interesting, as it is backed by several industrial partners. However, all the authors implicitly assume that the effective interfacial area are the same for the three chemical systems used to determine the mass transfer parameters. This assumption is likely to be true for the methods used to determine a_e and $k_G a_e$: both use chemical absorption with an excess of liquid phase reagent, and the saturation of certain liquid zones can be neglected. On the other hand, it is not clear to which extent a_e is reduced by the depletion of dissolved gas in stagnant or semi-stagnant liquid zones in the case of desorption, applied to determine $k_L a_e$.

Conclusions

Measurement methods of interfacial areas (a), gas- (k_G) and liquid-side (k_L) mass-transfer coefficients have been reviewed for packed absorption columns. The methods reviewed range from the earliest experiments to the most recent ones thus providing a broad overview of the possibilities and offering opportunities to reassess older methods in light of modern measurement techniques. In recent years, several authors have called for the standardization of measurement methods for absorption, and our work aims to contribute to this effort.

There exists a wide variety of techniques for specific area measurements. However, the various techniques do not all represent the same surfaces. Evaporation methods will give the true gas-liquid interfacial area whereas physical absorption or desorption methods will give an effective interfacial area which will be lower in value due to the existence of stagnant regions. It is important to clearly distinguish these different types of areas in order to use the appropriate one for column design. The most common method is one that is also recommended for standardization by several authors, namely the absorption of CO_2 into NaOH solutions. This system yields the effective area for chemical absorption. A new, albeit costly alternative is x-ray tomography which has the potential of providing very localized on top of global information.

In practice, k_G and k_L cannot be measured directly, but only from mass-transfer coefficients measurements of k_{Ga_e} and k_{La_e} after division by the appropriate effective area. Methods for determining the gas- or liquid-side mass-transfer coefficients are based on global flux measurements with systems that attempt to minimize the contribution of the resistance of the other phase to the measured global flux. For k_{Ga} , this can happen by evaporating a pure liquid, by the absorption of a highly soluble gas or by using a very fast chemical reaction which takes place on the gas-liquid interface (e.g., SO_2 and NaOH). For k_{La} , the gas side resistance is minimized by using poorly soluble solutes under conditions of absorption or desorption, such as with CO_2 , O_2 , or even toluene in water. Less frequently, chemical absorption is also used in different reaction regimes.

The treatment of internal and external end effects needs to be considered in order to evaluate the intrinsic mass transfer parameters of the packings. These can be negligible with tall beds, but significant with short beds. The latter ones are encountered specifically in the determination of k_{Ga} because the HTU_G in packings is generally small. Short beds are also encountered with k_{La} under absorption conditions due to the rapid approach to equilibrium. Since the magnitude of end effects can sometimes be very significant, it is recommended that they be determined by using multiple packed bed heights, or to make fluid composition measurements from fluid samples taken inside the packing or at least very close to the inlet and outlet planes. Even if end effects are eliminated, the mass transfer parameters can be influenced by the packed bed height. The most likely cause of this is liquid phase maldistribution that will modify the measured parameters, even if height dependency is not observed. By choosing a correct experimental setup, maldistribution can be avoided or reduced.

Finally, the suggestions for standardization of measurement methods were also reviewed. The recommendations of the authors cover test systems, experimental setup and procedures, analytical methods, and data treatment in order to ensure reliable and comparable measurement results. Standardization

will be a great step in reducing the scatter of data measurements among test centers and will lead to more reliable mass transfer parameter correlations.

Notation

Roman letters

- A = absorbed component, solute
- A^* = concentration of the solute at the surface of the liquid phase without chemical reaction, mol/m^3
- A^0 = concentration of the solute in the bulk liquid, mol/m^3
- a = specific area, m^2/m^3
- B = the reagent in the liquid phase
- B^0 = concentration of the reagent in the bulk liquid, mol/m^3
- C = factor by which the reaction increases the absorption capacity per unit volume of the liquid
- D = diffusion coefficient, m^2/s
- D_c = diameter of the column, m
- D_p = packing size, m
- E = enhancement factor
- G = molar flux of gas, $\text{mol}/(\text{m}^2\cdot\text{s})$
- H = packed bed height, m
- Ha = Hatta number
- He = Henry's law constant
- HETP = height equivalent of theoretical plate, m
- HTU = height of one transfer unit, m
- K_G = gas-side overall mass-transfer coefficient, $\text{mol}/(\text{m}^2\cdot\text{s})$
- K_L = liquid-side overall mass-transfer coefficient, $\text{mol}/(\text{m}^2\cdot\text{s})$
- k = rate constant ($\text{m}^{3(m+n)}/\text{mol}^{(m+n-1)}$)
- k_G = gas-side mass-transfer coefficient, $\text{mol}/(\text{m}^2\cdot\text{s})$
- $(k_Ga)_L$ = gas-side volumetric mass-transfer coefficient at the liquid superficial velocity corresponding to completely wetted packing, $\text{mol}/(\text{m}^2\cdot\text{s})$
- k_L = liquid-side mass-transfer coefficient, $\text{mol}/(\text{m}^2\cdot\text{s})$, in Figure 1: $1/\text{s}$
- $k_{L,R}$ = liquid-side mass-transfer coefficient in presence of a chemical reaction, $\text{mol}/(\text{m}^2\cdot\text{s})$
- k_R = reaction term, $1/\text{s}$
- L = mass flux of liquid, $\text{kg}/(\text{m}^3\cdot\text{h})$
- l = volume of liquid phase per unit volume of packing
- m = order of reaction with respect to the solute (section "Determination of the Effective Interfacial Area") equilibrium relation between gas and liquid phase mole fraction (elsewhere)
- n = order of reaction with respect to the liquid phase reagent
- NTU = number of transfer units
- p = coefficient in Eq. 30 (section "Determination of the Gas-Side Mass-Transfer Coefficient—Physical absorption") partial pressure of the solute in the bulk gas (elsewhere; Pa)
- q = coefficient in Eq. 30
- r = coefficient in Eq. 30
- Re = Reynolds number
- Sc = Schmidt number
- u = superficial velocity, m/s
- x = mole fraction in liquid phase
- y = mole fraction in gas phase

Greek letters

- α = coefficient in Eq. 30
- β = coefficient in Eq. 30
- γ = coefficient in Eq. 32
- γ_{DG} = ratio of the rates of absorption into reacting and CO_2 -free inert solution
- γ_{JD} = factor used by Joosten and Danckwerts²²
- η = effective part of a_{st}
- ν = the ratio of the reacting number of moles of B and A
- Φ = rate of absorption per unit volume, $\text{mol}/(\text{m}^3\cdot\text{s})$
- ϕ = rate of absorption per unit surface, $\text{mol}/(\text{m}^2\cdot\text{s})$

Subscripts

- cell = stirred cell
- dry = dry surface
- dyn = dynamic
- E = end effect

e = effective
 EE = external end effect
 G = gas phase
 g = geometrical
 i = interface, interfacial
 IE = internal end effect
 in = entering the column
 inf = infinitely fast reaction
 L = liquid phase
 OG = overall gas-side
 OL = overall liquid-side
 out = leaving the column
 st = static
 w = wetted

Superscripts

* = equilibrium
 ′ = measured

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