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# MASS TRANSPORT IN ELECTROLYTIC CELLS WITH GAS SPARGING

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**Abstract**—Mass transfer at a vertical gas sparged electrode with and without superimposed electrolyte flow has been investigated. The mass-transfer coefficient depends only on the gas voidage fraction, irrespective of the absolute values of the liquid flow velocity and the gas flow rate. The system has a strong similarity with turbulent free convection. The results can be represented by an analogous correlation in which the Grashof number, characteristic for free convection, is replaced by a modified Archimedes number:

$$Sh = 0.19(Sc\,Ar^*)^{1/3}.$$

## NOMENCLATURE

- $d$, distance between electrodes [cm];
- $D$, diffusion coefficient [$cm^2\,s^{-1}$];
- $g$, gravitational acceleration [$cm\,s^{-2}$];
- $k$, mass-transfer coefficient [$cm\,s^{-1}$];
- $l$, characteristic length [cm];
- $v_G$, amount of gas introduced into the cell per unit electrode (frit) area [$cm^3\,cm^{-2}\,s^{-1}$];
- $u_G$, superficial gas velocity [$cm^3\,cm^{-2}\,s^{-1}$];
- $u_E$, flow velocity of the electrolyte [$cm\,s^{-1}$];
- $u_0$, terminal rising velocity of an isolated bubble in an infinite medium [$cm\,s^{-1}$];
- $u_B$, rising velocity of the bubbles in a swarm [$cm\,s^{-1}$];
- $Ar$, Archimedes number, equation (1);
- $Ar^*$, modified Archimedes number, equation (3);
- $Sh$, Sherwood number, $Sh = k \cdot l/D$;
- $Sc$, Schmidt number, $Sc = v/D$;
- $Gr$, Grashof number, $Gr = l^3 \cdot g\Delta\rho/\rho_\infty v^2$.

Greek symbols

- $\chi_0$, specific conductivity of the liquid [$\Omega^{-1}$/cm];
- $\chi_{DISP}$, specific conductivity of the dispersion [$\Omega^{-1}$/cm];
- $\varepsilon$, gas voidage fraction (−);
- $\rho$, density [$g\,cm^{-3}$];
- $v$, kinematic viscosity [$cm^2\,s^{-1}$].

Subscripts

- l, liquid phase;
- g, gas phase.

## INTRODUCTION

IN ELECTROLYTIC cells, stirring by gas bubbles is a very efficient method for the enhancement of mass transfer [1,2]. Its application has been discussed mainly in connection with electrometallurgical processes [3,4]. We can distinguish between two cases:

(i) Gas evolving electrodes, where the bubbles are produced by an electrochemical reaction at the electrode itself; and

(ii) electrodes with gas sparging, where the gas is introduced from outside (e.g. through a porous plate [5]) or produced at the counter electrode [6,7].

On the basis of a penetration model Ibl and Venczel [8,9] have derived a correlation for describing mass transport at gas evolving electrodes. Vogt [10] finds a similar correlation in dimensionless form by a microconvection model, and Janssen [11,12] uses a hydrodynamic (macroconvection) approach.

Mass transport at electrodes with gas sparging has found relatively little attention and no general correlations for this system have been established until now. On the other hand considerably more work has been done in the field of heat transfer between dispersed two-phase systems and solid walls which is a quite similar situation [13–16], and we shall therefore apply the method used there in the treatment of the results of mass transport measurements at gas sparged electrodes carried out in our laboratory [1, 2, 5, 6]. Whereas one cannot find a satisfactory explanation for the stirring mechanism of gas bubbles when correlating the mass-transfer rate to the gas flow rate [5], a dimensionless correlation suitable for practical purposes shall be given here which is in agreement with a "natural convection" model describing the fluid motion caused by the bubbles.

## EXPERIMENTAL

Figure 1a shows schematically the cell used by Adam [5]. The gas (nitrogen) was introduced through a porous plate at the bottom of the cell between the vertical parallel electrodes. A different type of cell has been used in the study to which the present paper mainly refers [6]. We investigated the influence of gas bubbles generated by the counter electrode, whereby for practical reasons the electrolytic gas evolution was simulated by a vertical porous plate through which the gas (dry air) entered into the cell. The gas volume flow rate per unit

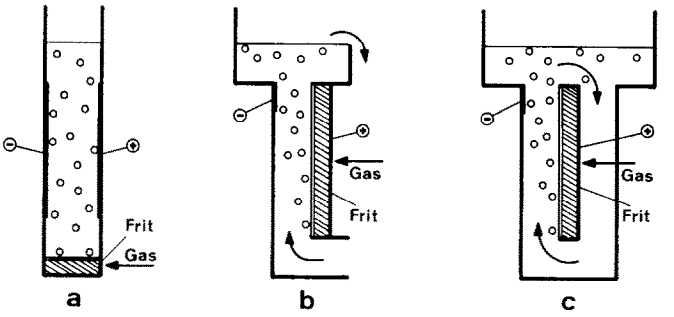


FIG. 1. Schematic representation of the cells: (a) Without electrolyte circulation; (b) External circulation; (c) Internal circulation.

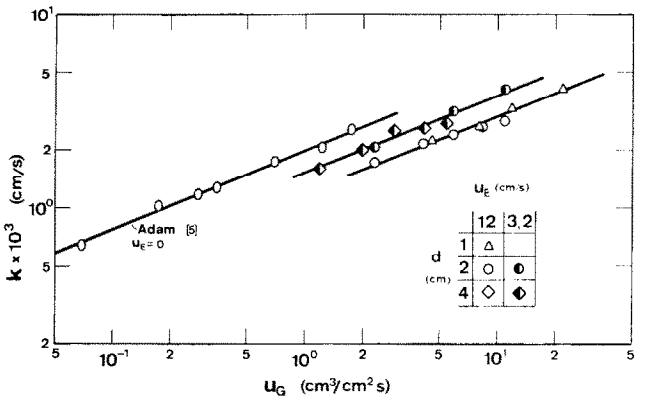


FIG. 2. Mass transfer coefficient $k$ vs superficial gas velocity $u_G$ for different electrolyte velocities $u_E$ and inter-electrode distances $d$.

electrode area could be varied between 0.17 and $0.82\,cm^3\,cm^{-2}\,s^{-1}$. Two different situations were investigated: With the arrangement shown in Fig. 1b a flow of the liquid could be superimposed on the motion caused by the gas bubbles by means of an external pump (external circulation). The height and the breadth of the porous electrode was 30 and 10 cm, respectively; the distance between the electrodes was 1, 2 and 4 cm, the electrolyte flow rate $u_E$ could be varied between 1.5 and $35.5\,cm\,s^{-1}$. Figure 1c shows a modification of this cell in which there is no external electrolyte flow but an internal circulation around the porous plate due to the gas lift effect (internal circulation). The maximum velocity was about $30\,cm\,s^{-1}$. The same electrode distances were used. Because an even distribution of the bubbles is realized only above a certain height which depends on electrode distance, gas flow rate and liquid velocity, the mass-transfer rates were measured only at the top segment of the working electrode (which consisted of several segments isolated from each other but kept at the same potential). Special attention had to be paid to the construction of the porous plate (uniform gas distribution) and to the design of the expansion zone above the electrodes (facilitation of the evacuation of the bubbles from the interelectrode gap). Details of the apparatus and the experimental technique used are given in [6].

The well known limiting current method with the electrolyte system $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ was used to measure the mass transfer rates [17]. The composition of the electrolyte was:

$$0.5\,M\,NaNO_3,\quad 0.2\,M\,NaOH,$$
$$0.01\,M\,K_4Fe(CN)_6,\quad 0.005\,M\,K_3Fe(CN)_6.$$

At 25°C the kinematic viscosity of the solution and the diffusion coefficient of the ferricyanide ion were $0.93\cdot10^{-2}\,cm^2\,s^{-1}$ and $8.13\cdot10^{-6}\,cm^2\,s^{-1}$, respectively. The working electrode was made of nickel, the porous plate anode of sintered steel.

In addition to the mass-transfer rate the gas voidage in the channel between the electrodes was measured by means of a conductivity method.†

## RESULTS

Figure 2 shows some typical results of the mass-transfer measurements. The mass transfer coefficient $k$ is plotted vs the superficial gas velocity $u_G$ for two different electrolyte flow velocities $u_E$ and three anode–cathode distances $d$. The distance between the electrodes apparently has no influence on the mass-transfer coefficient if one represents the results this way, the superficial gas velocity seems to be the

†The conductivity of dispersions of non-conducting particles has been studied by different authors [18, 19]. It was shown experimentally [6] that up to a gas voidage of 0.6 the specific conductivity of a bubble dispersion is given by the Maxwell correlation:

$$\frac{\chi_{DISP}}{\chi_0} = \frac{1-\varepsilon}{1+\varepsilon/2}.$$

relevant parameter. Also shown are some mass-transfer data obtained by Adam [5]. They show a similar behaviour although the mode of introducing the gas was different. They lie above the data of the present study due to the absence of a net electrolyte flow ($u_E = 0$) This confirms our findings concerning the dependence of mass transfer on the liquid flow velocity: In Fig. 3 the mass-transfer coefficient is plotted vs the liquid flow velocity (external circulation) for different superficial gas velocities. One finds that for a given gas velocity the mass transfer rate is lowered by increasing electrolyte flow. This

## DISCUSSION

We have seen in the preceding section that the macroscopic flow situation does not seem to be very relevant for mass transfer from a dispersed system to a solid wall. The fact that the mass transfer increases with the bubble concentration suggests that it is rather the motion of the bubbles which plays the dominant role. The fluid dynamics of dispersed two-phase systems are governed not only by inertia and viscous but also by gravitational forces, whereby in the case of gas bubbles in a liquid these forces are determined mainly by the properties of the liquid

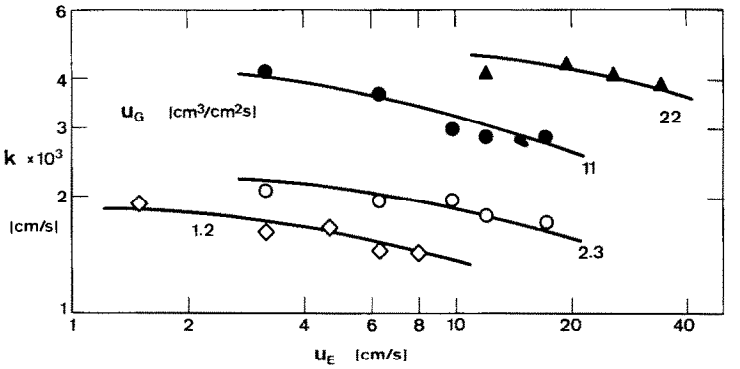


FIG. 3. Mass transfer coefficient $k$ vs electrolyte flow velocity $u_E$ for different superficial gas velocities $u_G$.

seems surprising at first sight, since the fluid flow should be supposed to assist convective mass transfer in a general way. However, the superimposed fluid flow increases the rising velocity of the bubbles which in turn results in an expansion of the bubble swarm and in a corresponding decrease of the voidage fraction.† The experimentally observed relationship between the voidage fraction, the gas and the electrolyte velocities is shown in Fig. 4. One finds that $\varepsilon$ depends on $u_G$ and $u_E$ in a rather similar way as the mass transfer coefficient $k$. This suggests that we plot $k$ as a function of the void fraction. This has been done in Fig. 5, and one can see that it is in fact possible to represent the results as a function of a single variable which combines the influence of the gas and of the liquid flow velocities. But also the results obtained without external circulation (cell 1c) can be represented in the same way (Fig. 6). A comparison of Fig. 5 and 6 shows that in both cases one obtains the same mass-transfer rate for a given void fraction, irrespective of the values of $u_G$ and $u_E$. It therefore seems that the flow behaviour in a bubble dispersion and thus the mass transport to a wall placed in such a dispersion are determined to a large extent by the volumetric voidage fraction of the gas.

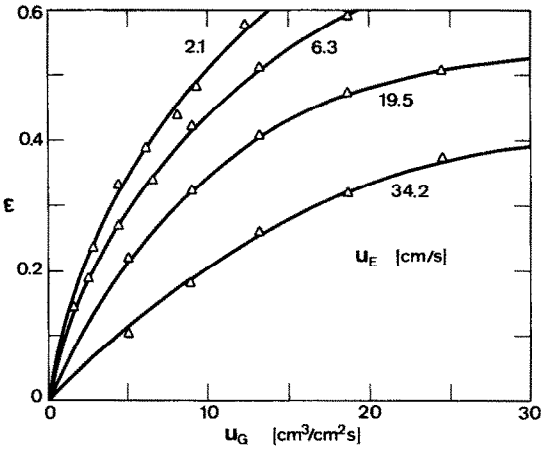


FIG. 4. Gas voidage $\varepsilon$ vs superficial gas velocity $u_G$ for different electrolyte velocities $u_E$.

[21]. The characteristic dimensionless group to be used for the description of bubble motion is the Archimedes number [22]

$$Ar = \frac{l^3 g\Delta\rho}{\nu^2\rho_\infty}. \quad (1)$$

The expression $g\Delta\rho = g(\rho_l - \rho_g)$ characterizes the buoyancy force acting on a single bubble. In the case of a bubble swarm with a gas voidage $\varepsilon$ it has to be replaced by $\varepsilon g\Delta\rho$. For the average density of the two-phase system we put:

$$\rho_\infty = (1-\varepsilon)\rho_l + \varepsilon\rho_g. \quad (2)$$

†After Nicklin [20] the rising velocity of bubbles in a swarm is given by

$$u_B = u_G/\varepsilon \quad \text{and} \quad u_B = u_G + u_E + u_0,$$

where $u_0$ is the rising velocity of an isolated bubble.

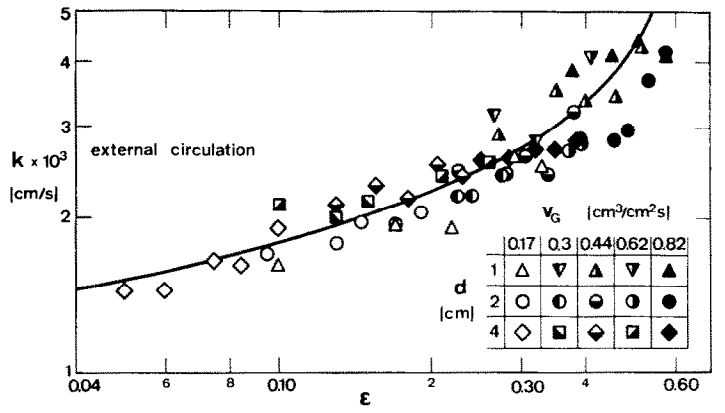


FIG. 5. Mass-transfer coefficient $k$ vs gas voidage $\varepsilon$; external circulation.

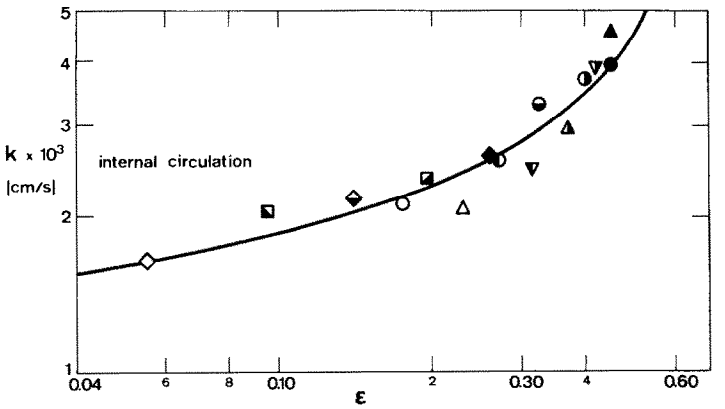


FIG. 6. Mass-transfer coefficient $k$ vs gas voidage $\varepsilon$; internal circulation. Symbols as in Fig. 5.

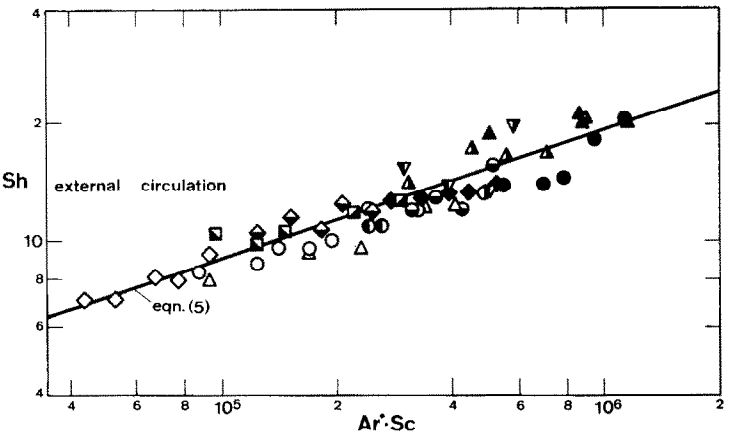


FIG. 7. Dimensionless representation of the mass-transfer results; external circulation. Symbols as in Fig. 5.

The second term on the right side of (2) can be neglected if we take into account that $\rho_g \ll \rho_l$. Thus the modified Archimedes number describing the motion of a bubble dispersion becomes:

$$Ar^* = \frac{l^3 g}{\nu^2} \cdot \frac{\varepsilon}{1-\varepsilon}. \tag{3}$$

It has been tried then to represent the experimental results by a dimensionless equation of the form

$$Sh = f(Ar^*, Sc). \tag{4}$$

Since no dependence of the mass-transfer coefficient on the height and the breadth of the channel between the electrodes could be found the bubble diameter has been used as the characteristic length in $Sh$ and $Ar^*$. The following correlation has been obtained from the experimental data:

$$Sh = 0.19(Sc\,Ar^*)^{1/3}. \tag{5}$$

Equation (5) is represented in Figs. 7 and 8 together with the experimental data.

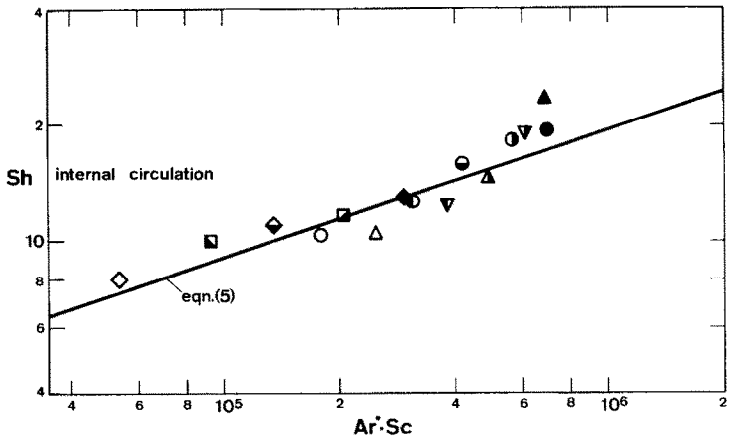


FIG. 8. Dimensionless representation of the mass-transfer results; internal circulation. Symbols as in Fig. 5.

Taking into account that the mass-transfer rate does not depend on the height of the electrode and the breadth of the interelectrode gap, and with the plausible assumption that besides these two geometric parameters the bubble diameter is the only relevant characteristic length, dimensional analysis yields that the mass-transfer correlation should contain no further dimensionless groups. Consequently the power 1/3 of $Ar^*$ indicates that the mass-transfer coefficient is also independent on the bubble diameter. However, the ideas of the stirring mechanism of bubbles outlined below justify its use in the formation of the dimensionless groups. It is noteworthy that equation (5) is practically identical with the correlations found for mass and heat transfer under turbulent free convection conditions [23–27], if one replaces the Archimedes by the Grashof number

$$Sh = \text{const.}(ScGr)^{1/3}. \qquad (6)$$

In fact the two groups are formed in a completely analogous way. The only distinction is that the density difference responsible for buoyancy results from a temperature or concentration gradient in one case, whereas in a two-phase system it is given by the different densities of the two phases. The motion of a bubble dispersion can thus be considered as a kind of natural convection. This analogy has already been discussed in connection with heat transfer between dispersed two-phase systems and solid walls [16, 23]. The analogy with turbulent free convection can be illustrated in a qualitative way by the following considerations [14] (Fig. 9): A rising bubble displaces liquid creating thus a velocity component $u_y$ perpendicular to the direction of motion. The velocity of the bubbles is usually large enough so that turbulent eddies are formed in the wake of the bubbles. This transverse motion of the liquid constitutes—in an analogous way as the fluctuations in "normal" turbulence—the major contribution to mass transport. There is thus some sort of micro-turbulence in the surroundings of the individual

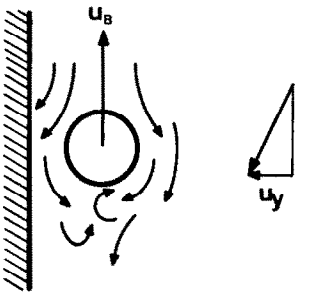


FIG. 9. Simplified representation of the flow situation around a rising bubble.

bubbles. With the plausible statement $k = f(u_y)$ and $u_y \sim u_B$, and taking into account that the rising velocity $u_B$ of the bubbles is described by the Archimedes number, we arrive at the result that mass transfer from a liquid stirred by rising bubbles to a vertical wall can be characterized by an Archimedes number.

The micro-turbulence model is sustained by the experimental finding that a superimposed electrolyte flow causes a decrease of the mass transfer rate. Indeed the overall fluid velocity increases, and one would expect a corresponding enhancement of mass transport, but on the other hand the bubble dispersion is expanded and the concentration of the turbulence promoting bubbles is diminished. Obviously this latter effect is compensating the other one. Of course this behaviour will be observed only as long as the superimposed velocity is not too large. Otherwise the bubbles will lose their influence on mass transport and the mass transfer coefficient will again increase with the flow velocity. The above mentioned finding shows also that the effects of two different stirring mechanisms—each of them enhancing mass transfer—need not necessarily be additive as in the case of gas evolving electrodes [28–30]. If they influence each other, as is the case here, they can act in opposite directions.

The success of the free convection model in describing mass transfer at gas sparged electrodes

suggests that it might be applicable also to the case of gas evolving electrodes. If we bear in mind that for gas evolution the expression $\varepsilon/(1-\varepsilon)$ appearing in the Archimedes number is proportional to the amount of gas evolved per unit time and thus to the current density $i$ [6, 31], we deduce from our mass transfer correlation (5) that the mass-transfer coefficient is proportional to $i^{1/3}$. In fact this exponent lies well in the range of values given in the literature [32]. Moreover, in the analogous situation of heat transfer under nucleate boiling conditions the model has proved to be suitable [31]. Recently Janssen [33] has proposed to treat mass transfer at gas evolving electrodes on the basis of a natural convection concept.

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## REFERENCES

1. N. Ibl, E. Adam, J. Venczel and E. Schalch, Stofftransport bei der Elektrolyse mit Gasrührung, *Chemie-Ingr-Tech.* **43**, 202–215 (1971).
2. N. Ibl. R. Kind and E. Adam, Mass transfer at electrodes with gas stirring, *An. Quim.* **71**, 1008–1016 (1975).
3. V. A. Ettel, B. V. Tilak and A. S. Gendron, Measurement of cathode mass transfer coefficients in electrowinning cells, *J. Electrochem. Soc.* **121**, 867–872 (1974).
4. W. W. Harvey, M. R. Randlett and K. I. Bangerskis, Elevated current density electrowinning of superior quality copper from high-acid electrolyte, Ledgemont Lab. Kennecott Copper Corp. Techn. Report 409 (1975).
5. E. Adam, Zur Kenntnis des Stofftransportes an Gasblasenbespülten Elektroden und deren Optimierung, Diss. Nr. 4047, ETH Zürich (1967).
6. L. Sigrist, Dissertation ETH Zürich Nr 6286 (1978).
7. S. Mohanta and T. Z. Fahidy, The effect of anodic bubble formation on cathodic mass transfer under natural convection conditions, *J. Appl. Electrochem.* **7**, 235–238 (1977).
8. J. Venczel, Ueber den Stofftransport an gasentwickelnden Elektroden, Diss. Nr. 3019, ETH Zürich (1961).
9. N. Ibl. and J. Venczel, Untersuchung des Stofftransportes an gasentwickelnden Elektroden, *Metalloberfläche* **24**, 365–374 (1970).
10. H. Vogt, A Dimensionless Equation for Mass Transfer at Gas Evolving Electrodes, Paper presented at the 27th meeting of the International Society of Electrochemistry, Zürich (1976).
11. L. J. J. Janssen and J. G. Hoogland, The effect of electrolytically evolved gas bubbles on the thickness of the diffusion layer II, *Electrochim. Acta* **18**, 543–550 (1973).
12. L. J. J. Janssen, Mass transfer at gas evolving electrodes, *Electrochim. Acta* **23**, 81–86 (1978).
13. R. B. MacMullin, K. L. Mills and F. N. Ruehlen, Enhancement of liquid film heat transfer by electrolytic gas evolution, *J. Electrochem. Soc.* **118**, 1582–1587 (1971).
14. W. Kast, Untersuchungen zum Wärmeübergang in Blasensäulen, *Chemie-Ingr-Tech.* **35**, 785–788 (1963).
15. F. O. Mixon, W. Y. Chon and K. O. Beatty, The effect of electrolytic gas evolution on heat transfer, *Chem. Engng Prog. Symp. Ser.* **56**, 75–81 (1960).
16. A. Mersmann, Zum Wärmeübergang zwischen dispersen Zweiphasensystemen und senkrechten Heizflächen im Erdschwerefeld, *Verfahrenstechnik* **10**, 641–645 (1976).
17. P. Grassmann, N. Ibl and J. Trüb, Elektrochemische Messung von Stoffübergangszahlen, *Chemie-Ingr-Tech.* **33**, 529–533 (1961); T. Mizushina, The electrochemical method in transport phenomena, in *Advances in Heat Transfer*, edited by T. F. Irvine, Vol. 7, pp. 87–161. Academic Press, New York (1971).
18. R. E. De la Rue and C. W. Tobias, On the conductivity of dispersions, *J. Electrochem. Soc.* **106**, 827–833 (1959).
19. J. C. R. Turner, Two phase conductivity, *Chem. Engng Sci.* **31**, 487–492 (1976).
20. D. J. Nicklin, Two-phase bubble flow, *Chem. Engng Sci.* **17**, 693–702 (1962).
21. P. Grassmann, *Physikalische Grundlagen der Chemieingenieurtechnik*, chap. 10. Sauerländer Aarau (1961).
22. P. Grassmann and A. Reinhart, Zur Ermittlung der Sinkgeschwindigkeit von Tropfen und der Steiggeschwindigkeit von Blasen, *Chemie-Ingr-Tech.* **33**, 348–349 (1961).
23. A. Mersmann, Zum Wärmeübergang in Blasensäulen, *Chemie-Ingr-Tech.* **47**, 869–908 (1975).
24. G. D. Raithby and K. G. T. Hollands, *Adv. Heat Transfer* **11**, 295 (1975).
25. F. A. Hollands, *Heat Transfer*. Heinemann, London (1970).
26. A. A. Wragg, Free convection mass transfer at horizontal electrodes, *Electrochim. Acta* **13**, 2159–2165 (1968).
27. E. J. Fenech and C. W. Tobias, Mass transfer by free convection at horizontal electrodes, *Electrochim. Acta* **2**, 311–325 (1960).
28. M. D. Birkett and A. T. Kuhn, Combined effects in mass transfer to a planar electrode, *Electrochim. Acta* **22**, 1427–1429 (1977).
29. T. R. Beck, A contribution to the theory of electrolytic chlorate formation, *J. Electrochem. Soc.* **116**, 1038–1041 (1969).
30. H. Vogt, Mass transfer at gas evolving electrodes with superposition of hydrodynamic flow, *Electrochim. Acta* **23**, 203–205 (1978).
31. N. Zuber, Nucleate boiling: The region of isolated bubbles and the similarity with natural convection, *Int. J. Heat Mass Transfer* **6**, 53 (1963).
32. I. Roušar and V. Cezner, Transfer of mass or heat to an electrode in the region of hydrogen evolution, *Electrochim. Acta* **20**, 289–293, 295–299 (1975).
33. L. J. J. Janssen, Mass transfer at gas evolving electrodes, Paper presented at the 29th meeting of the International Society of Electrochemistry, Budapest (1978).

## TRANSPORT DE MATIERE DANS UNE CELLULE ELECTROLYTIQUE AVEC BARBOTAGE DE GAZ

**Résumé**—On étudie l'influence du barbotage de gaz sur le transfert de matière autour d'une électrode verticale avec et sans circulation de l'électrolyte. Le coefficient de transfert massique ne dépend que de la fraction volumique du gaz, et non pas des valeurs absolues de la vitesse du liquide et du débit de gaz. Le système a une forte similitude avec la convection naturelle turbulente. Les résultats peuvent être représentés par une relation analogue, dans laquelle le nombre de Grashof, caractérisant la convection naturelle, est remplacé par un nombre d'Archimède modifié:

$$Sh = 0{,}19(Sc\,Ar^*)^{1/3}.$$

## STOFFTRANSPORT IN ELEKTROLYSEZELLEN MIT GASBLASENRÜHRUNG

**Zusammenfassung**—Es wurde der Stofftransport an einer gas-blasenbespülten senkrechten Elektrode mit und ohne überlagerter Elektrolyströmung untersucht. Der Stoffübergangskoeffizient hängt nur vom volumetrischen Gasgehalt ab, unabhängig von den Absolutwerten der Strömunggeschwindigkeit und des Gasdurchsatzes. Das System weist eine starke Aehnlichkeit mit der turbulenten natürlichen Konvektion auf. Die Resultate lassen sich durch eine analoge Beziehung darstellen wobei an die Stelle der bei der freien Konvektion verwendeten Grashofzahl eine modifizierte Archimedeszahl tritt:

$$Sh = 0{,}19(ScAr^*)^{1/3}$$

## ПЕРЕНОС МАССЫ В ЭЛЕКТРОЛИТИЧЕСКИХ ЯЧЕЙКАХ С БАРБОТАЖЕМ ГАЗА

**Аннотация** — Исследован перенос массы на вертикальном электроде с обдувом газа при наличии и отсутствии течения электролита. Коэффициент переноса массы зависит только от объёмной доли газовой фазы и не зависит от абсолютных значений скорости течения жидкости и газа. Рассматриваемая система аналогична системе с турбулентной свободной конвекцией. По аналогии результаты можно описать соотношением, в котором число Грастофа для свободной конвекции заменяется модифицированным числом Архимеда

$$Sh = 0{,}19(ScAr^*)^{1\ 3}$$