

MASS TRANSFER AT GAS EVOLVING ELECTRODES WITH SUPERPOSITION OF HYDRODYNAMIC FLOW

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Abstract—Mass transfer at gas evolving electrodes with additional major hydrodynamic liquid flow is influenced by two phenomena: effects directly resulting from the generated bubbles and effects by high liquid velocity parallel to the electrode surface. For the case of superposition of both mechanisms, being of great industrial importance, a method is presented to quantitatively describe mass transfer.

NOMENCLATURE

A	electrode area
C	factor in eq. (1)
$d = 4 S/U$	hydraulic diameter of the duct
D	diffusivity
f	Fanning friction factor
l	length of the duct
m, n	exponents
\dot{n}	molar flow rate
S	area of flow cross section
U	wetted perimeter
\dot{V}_G	volumetric rate of gas evolution
w	mean velocity
α	heat transfer coefficient
β	mass transfer coefficient
δ_N	Nernst diffusion layer thickness
ν	kinematic viscosity
$Re = wd/\nu$	Reynolds number
$Sc = \nu/D$	Schmidt number
$Sh = \beta d/D$	Sherwood number

THE PROBLEM

Research on mass transfer at gas evolving electrodes was until now only concerned with the case of essentially quiescent liquid or liquid with slight hydrodynamic flow caused by shear forces of rising bubbles. The case of considerable two-phase flow rates parallel to the electrode effecting the mass transfer at gas evolving electrodes did not receive proper attention. Such conditions occur in some technical applications, where the height of electrodes and a high gas evolving cd result in two-phase flow of great extent or where high flow rates are provided by additional pumping. One example is chlorate electrolysis, where recent technical improvements were based on the benefit of high electrolyte circulation through the cell[1-3].

Mass transfer at gas evolving electrodes is governed by two phenomena acting simultaneously:

1. Liquid flow parallel to the electrode surface influences mass transfer by the velocity distribution near the wall. This is the well-known phenomenon of macroconvective mass transfer. The extent of its influence on mass transfer is not related to events directly connected with gas evolution.
2. Microconvective mass transfer is connected with the bubbles adhering to the electrode. Liquid in the vicinity of the adhering bubble is pushed away by the growth of the bubble diameter, resulting in

a periodical disturbance of the diffusion layer with an increase of mass transfer.

Both phenomena superpose and jointly influence mass transfer. When they are of the same order of magnitude the macroconvective influence can no longer be overlooked. Though each of the mechanisms can be described separately, no method for predicting the effects of superposition yet exists.

As several types of gas evolution are known, it is emphasized that gas evolution as dealt herewith is always nucleate gas evolution. This is the only case where a superposition is of practical interest.

PURE MACROCONVECTION

If gas generating cd is not extremely low, macroconvection can only exercise an influence at turbulent flow condition. Mass transfer equations for pure turbulent macroconvection through ducts are available, such as the improved Pethukov-Popov heat transfer equation[4], transformed into a mass transfer equation:

$$Sh = \frac{fC}{2} \frac{ReSc}{1.07 + 12.7(Sc^{2/3} - 1)(f/2)^{0.5}} \times \left(1 - \frac{180}{Re^{0.75}}\right) \times \left[1 + \left(\frac{d}{l}\right)^{2/3}\right] \quad (1)$$

The factor C is borrowed from investigations with heat transfer by Stephan[5]: $C = 1$ for circular ducts, $C = 0.9$ for flow between narrow parallel plates as applies to the common cell arrangement. The equation (like others for single-phase flow[6]) claims an error of only a few percent.

PURE MICROCONVECTION

Much lower accuracy must be ascribed to the available equations for microconvective mass transfer. Empirical equations were presented by Roald and W. Beck[7], by Venzel[8] and Ibl[10], and by T. R. Beck[11], and are all of either the type

$$\beta \sim \left(\frac{\dot{V}_G}{A}\right)^m \quad (2)$$

or

$$\delta_N \sim \left(\frac{\dot{V}_G}{A}\right)^{-m}; \quad \beta \sim D \left(\frac{\dot{V}_G}{A}\right)^m. \quad (3)$$

An equation based on a theoretical concept was developed by Ibl and Venczel[8-10] and later on modified by Roušar[12, 13]. A further theoretical approach was presented by Vogt[14, 15].

SUPERPOSITION

To consider simultaneous macro- and microconvection, Beck[11] proposed an addition of both mass transfer coefficients calculated separately:

$$\beta = \beta_1 + \beta_2. \quad (4)$$

Simple addition of the mass transfer coefficients of the single mechanisms implies that both mechanisms are completely independent of each other. This concept cannot stand in confrontation to an analysis of the phenomena occurring when bubble formation and macroconvection work simultaneously.

A quiescent liquid is considered at first. At very low current densities of the gas generating reaction, the supersaturation of the liquid with gas is too small to allow bubble formation. Under steady-state condition the concentration profile near the electrode is maintained by mere diffusion of the dissolved gas into the bulk of liquid. When the cd is increased, the supersaturation of the liquid exceeds a lower limit sufficient for gas evolution and the first isolated bubbles are formed at the electrode. Liquid is set in motion by the shear forces caused by the departing and rising bubbles. Macroconvective mass transfer begins to superpose the microconvective one. In the vicinity of the adhering bubbles mass transfer is governed by the phenomena related to the microconvection caused by individual bubbles. On the rest of the electrode area, macroconvective flow remains decisive. With increase of cd , the number of simultaneously adhering bubbles is enlarged and the influence of microconvective mass transfer increases at the expense of the macroconvective one. Further increase of the cd finally results in a sole influence of microconvective mass transfer. The result is the same for forced macroconvection existing from the very beginning of gas evolution.

The above model is suggested by the behaviour which has been repeatedly observed for heat transfer in nucleate boiling[16, 17] and which is qualitatively illustrated in Fig. 1, shown for two macroconvective velocities. Each curve can be divided into three sections. In the lowest range "a" macroconvection only is effective. Heat transfer is quantitatively described by single-phase equations. Bubbles begin to form at "A". Vapor flow rate increases with enlarged superheating of the liquid. Curve "b" represents the range of simultaneous influence of macroconvection and of microconvection. At "c" nucleate boiling heat transfer is fully developed and the macroconvective velocity is virtually of no influence. The effect of the macroconvection decreases in the same extent as the number of adhering vapor bubbles grows. On this leading idea the derivation of a heat transfer equation by Nagel[18] was based.

Furthermore, a direct interaction between the two mechanisms occurs: Macroconvection influences the

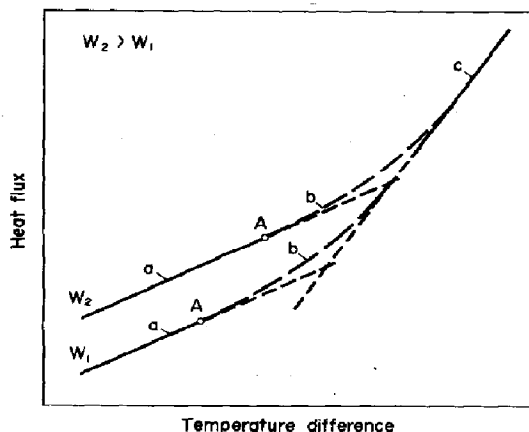


Fig. 1. Heat flux as function of the temperature difference between wall and bulk of liquid in nucleate boiling for different macroconvective velocities. (a) Range of single-phase heat transfer; (b) intermediate range of superposition; (c) range of fully developed nucleate boiling.

departure diameter of the gas or vapor bubbles by interfering with the balance of adhesion and buoyancy forces in such a way that increasing microconvection results in diminishing the departure diameter. This was experimentally confirmed by Kadija[19] for gas bubbles evolved under electrolysis condition on a rotating disc electrode. A corresponding finding for bubbles generated in nucleate boiling was reported by Koumoutsos[20]. Investigations by Abdelmessih[21] in slightly subcooled liquid showed a decreased maximum bubble diameter with increased liquid velocity.

It appears to be a rough approximation only to describe mass transfer at gas evolving electrodes with additional single-phase convection by simple addition of macro and microconvective effects.

Because of the analogy of the two transport phenomena it is useful also for quantitative consideration of mass transfer to refer to the results for nucleate boiling heat transfer, where research is much more advanced in comparison to gas evolving electrodes. It was also in the field of heat transfer that the problem of superposition arose and was handled in different ways.

McAdams[22] disregarded the mutual influence of macro- and microconvective heat transfer and proposed to use only the higher value of the two heat transfer coefficients:

$$\begin{aligned} \alpha &= \alpha_1 \text{ for } \alpha_1 > \alpha_2, \\ \alpha &= \alpha_2 \text{ for } \alpha_2 > \alpha_1. \end{aligned} \quad (5)$$

α_1 and α_2 are the heat transfer coefficients calculated separately for pure macro- and microconvection, respectively. McAdams himself called this procedure "slightly conservative". Rohsenow[17] proposed a simple addition to get the combined heat transfer coefficient in the way Beck[11] later did for mass transfer:

$$\alpha = \alpha_1 + \alpha_2. \quad (6)$$

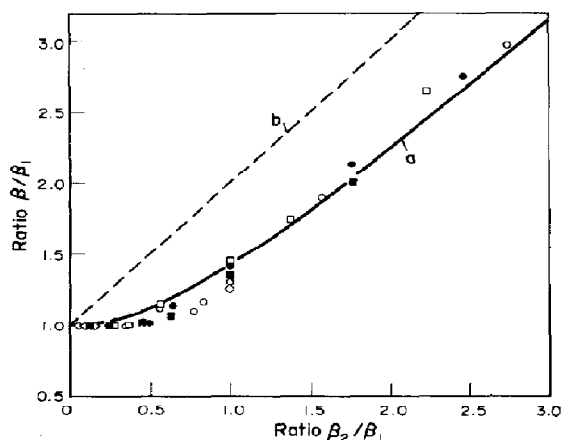


Fig. 2. Comparison of the combined mass transfer coefficient according to (8) with experimental data of Roald and Beck[7]. (a) Equation (8), (b) Equation (4). Rotation speed [min⁻¹]: ○, 200; ●, 380; □, 947; ■, 2880; ◇, 6400.

The equation was further improved by Kutateladze[23]

$$\alpha = (\alpha_1^n + \alpha_2^n)^{1/n} = \alpha_1 \left[1 + \left(\frac{\alpha_2}{\alpha_1} \right)^n \right]^{1/n} \quad (7)$$

by setting $n = 2$ (instead of $n = 1$). Good agreement with experimental results was reported[24]. Evaluation of comprehensive experimental data obtained by Brauer and communicated by Müller[16] confirms the practical fit of (7) for boiling conditions.

It is obvious to make use of the analogy between heat and mass transfer and to adapt the best equation for the superposition of macro- and microconvective mass transfer at gas evolving electrodes proposing

$$\beta = \beta_1 \left[1 + \left(\frac{\beta_2}{\beta_1} \right)^2 \right]^{0.5} \quad (8)$$

The subscripts refer again to pure micro- and macroconvection, respectively.

To test (8) experimental results obtained by Roald and Beck[7] are suitable. The authors studied the dissolution of magnesium in hydrochloric acid, a situation corresponding to that at gas evolving electrodes under electrolysis conditions. The similarity is supported by the good fit of those data which apply to negligible macroconvection with results obtained by Venczel[8] for electrolytic gas evolution. Roald and Beck[7] carried out their experiments in an agitated vessel, where the rotation speed of the agitator was varied up to 6400/min. Due to the wide limits of parameter variation these data represent the most useful ones available at present. A representative selection of them is shown in Fig. 2 together with (8). The standard deviation is smaller than 6%. The agreement is satisfactory with regard to the poor accuracy of the available mass transfer equations for nucleate gas evolution.

It is instructive to note that recently a theory for superposition of the phenomena at nucleate boiling was developed by Lemmert and Chawla[25] for re-

placement of the empirical relation (7). Following the analogy, one must expect that (8) presented here might be only preliminary, if it is at all felt necessary to improve and complicate it.

It is worth mentioning that (7) does no longer hold, if the vapor content in the two-phase system amounts to values higher than about 50%. In this case heat transfer depends no longer on vapor volume generated per time and surface area, but on the two-phase flow velocity, vapor content and geometry of the duct[26]. One must expect that under such conditions (8), too, loses its validity. Nevertheless, this range is usually of no importance for nucleate gas generation, as such a high gas content in the electrolyte is avoided if possible because of the considerable voltage drop.

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REFERENCES

1. Ger. Pat. 957937, Krebs & Co. (1957).
2. J. Fleck, *Chemie-Ingr-Tech.* **43**, 173 (1971).
3. Ger. Offenlegungsschr. 2248552, Hooker Chem. Corp. (1973).
4. B. S. Pethukov and V. N. Popov, *High Temp.* **1**, 69 (1963).
5. K. Stephan, *Chemie-Ingr-Tech.* **34**, 207 (1962).
6. H. Hausen, *Wärme-Stoffübertr.* **7**, 222 (1974).
7. B. Roald and W. Beck, *J. electrochem. Soc.* **98**, 277 (1951).
8. J. Venczel, Über den Stofftransport an gasentwickelnden Elektroden. Diss. ETH Zürich Nr. 3019 (1961).
9. N. Ibl and J. Venczel, *Metalloberfläche* **24**, 365 (1970).
10. N. Ibl, *Chemie-Ingr-Tech.* **43**, 202 (1971).
11. T. R. Beck, *J. electrochem. Soc.* **116**, 1038 (1969).
12. I. Roušar and V. Cezner, *Electrochim. Acta* **20**, 289 (1975).
13. I. Roušar, J. Kačín, E. Lippert, F. Šmirous and V. Cezner, *Electrochim. Acta* **20**, 295 (1975).
14. H. Vogt, Paper No. 51 presented at the ISE meeting, Zürich (1976).
15. H. Vogt, Ein Beitrag zum Stoffübergang an gasentwickelnden Elektroden. Diss. Universität Stuttgart (1977).
16. F. Müller, *Wärmeübergang bei der Verdampfung unter hohen Drücken*. VDI-Forschungsh. 522. VDI-Verlag: Düsseldorf (1967).
17. W. M. Rohsenow, *Developments in Heat Transfer*. M.I.T. Press, Cambridge, Mass. (1964).
18. O. Nagel, *Chemie-Ingr-Tech.* **35**, 179 (1963).
19. I. V. Kadija, B. Z. Nikolić and A. R. Despić, *J. electroanal. Chem. interf. Electrochem.* **57**, 35 (1974).
20. N. Koumoutsos, R. Moissis and A. Spyridonos, *Trans. ASME—J. Heat Transfer* **90**, 223 (1968).
21. A. H. Abdelmessih, F. C. Hooper and S. Nangia, *Int. J. Heat Mass Transfer* **15**, 115 (1972).
22. W. H. McAdams, W. E. Kennell, C. S. Minden, R. Carl, P. M. Picornell and J. E. Dew, *Ind. Engng Chem.* **41**, 1945 (1949).
23. S. S. Kutateladze, *Int. J. Heat Mass Transfer* **4**, 31 (1961).
24. S. S. Kutateladze, *Fundamentals of Heat Transfer*. Arnold, London (1963).
25. M. Lemmert and J. M. Chawla, Paper No. G 5-1 presented at GVC/AIChE Joint Meeting Munich (1974).
26. J. M. Chawla, *Chemie-Ingr-Tech.* **44**, 118 (1972).