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Mass transfer characteristics of electrochemical reactors employing gas evolving mesh electrodes

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Mass transfer rates were measured at a single screen and a fixed bed of closely packed screens for the simultaneous cathodic reduction of $K_3Fe(CN)_6$ and anodic oxidation of $K_4Fe(CN)_6$ in alkaline solution with H_2 and O_2 evolution, respectively. Variables studied were gas discharge rate, number of screens per bed and position of the electrode (vertical and horizontal). For single screen electrodes, the mass transfer coefficient was related to the gas discharge rate by the equations:

$$K = aV^{0.190}, \text{ for } H_2 \text{ evolving electrodes,}$$

$$K = aV^{0.469}, \text{ for } O_2 \text{ evolving electrodes.}$$

Electrode position was found to have no effect on the rate of mass transfer for single and multiscreen electrodes in the case of H_2 and O_2 evolution. Mass transfer coefficients were found to increase with an increasing number of screens per bed in the case of H_2 evolution, while in the case of O_2 evolution the mass transfer coefficient decreased with an increasing number of screens per bed. A mathematical model was formulated to account for the behaviour of the H_2 evolving electrode which, unlike the O_2 evolving electrode, did not obey the penetration model. Power consumption calculations have shown that the beneficial effect of mass transfer enhancement is outweighed by the increase in the voltage drop due to gas evolution in the bed electrode.

Nomenclature

a, $\bar{a}$	constants
A	electrode area, cm^2
C	concentration, $mol\,cm^{-3}$
D	diffusivity, $cm^2\,s^{-1}$
F	Faraday's constant
g	gravitational acceleration $cm\,s^{-2}$
Gr	Grashof number, $Gr = (gL^3/\nu^2)(\Delta\rho/\bar{\rho})$
i	current, A
K	mass transfer coefficient, $cm\,s^{-1}$
L	electrode length, cm
Sc	Schmidt number, $Sc = \mu/\rho D$
Sh	Sherwood number, $Sh = KL/D$
V	gas volume discharge rate, $cm^3\,cm^{-2}\,min^{-1}$
Z	number of electrons in reaction
ϵ	void fraction
μ	viscosity, $g\,cm^{-1}\,s^{-1}$
ν	kinematic viscosity $cm^2\,s^{-1}$
ρ	density, $g\,cm^{-3}$
g	gas phase (subscript)
l	liquid phase (subscript)

1. Introduction

Industrial electrolytic processes often involve diffusion controlled reactions which take place with a current efficiency below 100% owing to the simultaneous evolution of H_2, O_2 or Cl_2 at the working electrode. Gas evolution may affect the performance of electrochemical reactors, e.g. by increasing the ohmic drop in the reactor and hence the power consumption, or through the stirring effect by enhancing the mass transfer processes at the electrode surface. Electrochemical reactor

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designers are faced with the task of minimizing the deleterious effects of gas evolution and maximizing its beneficial effects. To this end considerable work has been done both on the effect of gas evolution on ohmic drop and on the rate of mass transfer. In the area of mass transfer most investigations have been carried out on vertical and horizontal plates. Little has been done on other geometries such as screen electrodes despite the increasing importance of these electrodes in building electrochemical reactors [1–6] to take advantage of their high surface area per unit volume. Previous mass transfer studies on screens and screen arrays have concentrated on the natural [7–9] and forced convection [10–24] mass transfer behaviour under non-gas evolving conditions. However, Fouad and Sedahmed [25] did study rates of mass transfer at H_2 evolving electrodes made of a single screen and of an array of separated screens. The object of the present work is to study the effect of H_2 and O_2 evolution on the rate of mass transfer at externally unstirred gas evolving electrodes made of a single screen and an array of closely packed screens.

Previous studies on gas evolving electrodes have revealed the fact that mass transfer at gas evolving electrodes is a complex phenomenon [26] which is difficult to analyse theoretically in view of the many factors involved in the process. However, analogous work on boiling heat transfer has led to the presentation of different theories to account for the mechanism of mass transfer at gas evolving electrodes. In general gas evolution can be considered to accelerate mass transfer by three means:

1. The ascending bubbles cause a bulk movement of the liquid at the electrode surface (hydrodynamic or macroconvection model) [27, 28].
2. When a bubble separates from the interface it leaves a void, into which fresh solution flows, thus supplying the dissolved species to the electrode (penetration or renewal model) [29].
3. Liquid in the vicinity of the adhering bubble is pushed away by the growth of the bubble diameter, resulting in a periodic disturbance of the diffusion layer with an increase of mass transfer (microconvection model) [30].

Both the penetration model and the microconvection model lead to the equation

$$K = aV^{0.5}. \qquad (1)$$

The hydrodynamic boundary layer model is only a qualitative model.

2. Experimental technique

The apparatus used (Fig. 1) consisted of a cell and electrical circuit. The cell was made of a 1 dm^3 cylindrical glass container of 10.5 cm inner diameter (i.d.), divided into two compartments by a tight cylindrical porous diaphragm of 4.7 cm i.d. made of synthetic fabric. The contact between the bottom of the diaphragm and the bottom of the container was sealed with wax. The inner electrode was composed of a single or a number of closely spaced stainless screens mounted horizontally or vertically on a 2 mm nickel wire, which acted as an electrode holder and a current feeder. This wire was electrically insulated using epoxy resin except

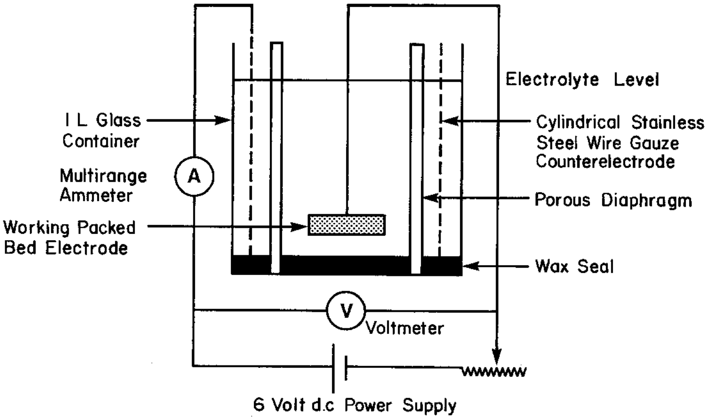

Fig. 1. Cell and electrical circuit.

at the contact with the screens. Each screen was rectangular in shape (3 cm × 3 cm) and had a mesh number of 20 square apertures per linear inch, wire diameter of 0.375 mm, porosity of 0.75 and area density of $30\,\mathrm{cm^2\,cm^{-3}}$. The outer electrode was a cylindrical stainless steel screen of 10 cm diameter.

Current was drawn from a 6 V d.c. power supply with a voltage regulator and measured on a multi-range ammeter. Cell voltage was measured by a voltmeter connected in parallel with the cell.

Before each run the inner electrode was degreased with trichloroethylene and washed with alcohol and distilled water. The cell was filled with electrolyte up to a height of 7 cm; care was taken that the level of the electrolyte was the same in both compartments. The solution was composed of $0.1\,\mathrm{mol\,dm^{-3}}$ potassium ferricyanide, $0.1\,\mathrm{mol\,dm^{-3}}$ potassium ferrocyanide and $2\,\mathrm{mol\,dm^{-3}}$ sodium hydroxide as a supporting electrolyte to eliminate the transfer of the electroactive ion by electrical migration. Electrolysis was conducted at 25° C for a time sufficient to produce about 5% concentration change. After each run, the solution in the inner compartment was stirred well and a sample was taken for the analysis of ferri- and ferrocyanide ions. Ferricyanide ion was determined by iodometry [31] while ferrocyanide ion was determined by titration against standard potassium permanganate solution [31]. The mass transfer coefficient was calculated using the simple equation

$$\frac{i}{AZF} = KC. \tag{2}$$

The current (i) consumed in reducing ferricyanide ion or oxidizing ferrocyanide ion was calculated using Faraday's law and the analytically determined decrease in ferricyanide or ferrocyanide ion concentration. The gas discharge rate was calculated by subtracting the current consumed in reducing or oxidizing ferricyanide or ferrocyanide ions from the total current passing and then applying Faraday's law to obtain the mass of H_2 or O_2 evolved per second. This mass was converted into volume using the gas law. The true surface area (A) of the screens was calculated from the number of apertures per linear cm and the wire diameter using the method of Armour and Cannon [32].

Based on previous studies on natural convection mass transfer at vertical and horizontal arrays of closely spaced screens, [7, 8] the maximum number of screens per array was limited to 7 to avoid nonuniformity in potential and current distribution within the array. Under the present conditions, visual observations showed that gas evolution started immediately after the limiting current at different parts of the array (horizontal or vertical). The study of Alkire and Gracon [11] has shown that current distribution is almost uniform inside beds of screens of small thickness (similar to that used in the present work) at different solution flow rates.

3. Results and discussions

Figure 2 shows the effect of H_2 and O_2 discharge rates on the mass transfer coefficient of the reduction of $K_3Fe(CN)_6$ and the oxidation of $K_4Fe(CN)_6$, respectively, at horizontal and vertical single screens. The data can be represented by the following equations:

$$K = aV_{H_2}^{0.190} \tag{3}$$

$$K = aV_{O_2}^{0.469}. \tag{4}$$

For the H_2 evolving electrode the exponent 0.19 compares favourably with the value obtained by Fouad and Sedahmed [25] (0.17) for a single screen electrode. For the O_2 evolving electrode the exponent 0.469 agrees reasonably with the prediction of 0.50 for the penetration model [29]. The difference in mass transfer behaviour between the H_2 evolving electrode and the O_2 evolving electrode may be attributed to the difference in bubble size of the two gases. Janssen and Hoogland [27] found that in alkaline solutions O_2 bubbles are much larger than H_2 bubbles owing to their higher ability to coalesce in alkaline solutions. The present results are consistent with previous studies [25–30, 33–44] on gas evolving electrodes where the $\log K/\log V$ slope ranges from 0.15 to 0.87 depending on the nature of the gas and electrolyte, current density range and electrode geometry. A review of these studies indicates that in general the penetration model and the microconvection model do not apply under two sets of conditions:

(i) conditions leading to the production of small noncoalescent bubbles at low gas discharge rates, e.g. the production of H_2 from alkaline solu-

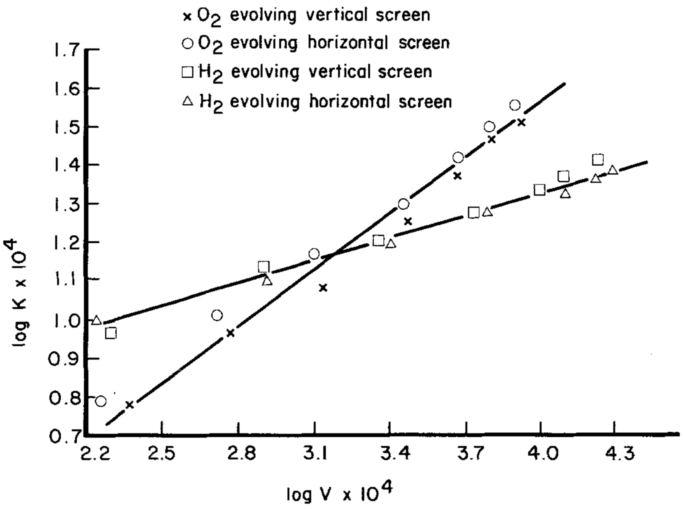

Fig. 2. Effect of gas discharge rate on the mass transfer coefficient at single screen electrode.

tion at relatively low current densities [27]. Under such conditions the log$K$/log V slope is much less than the value 0.5 given by the penetration model.

(ii) conditions leading to excessive coalescence of bubbles at the electrode surface and thence detached from the electrode, e.g. the production of O_2 from alkaline solution at high current densities [27]. Under these conditions the log$K$/log V slope is much higher than the value 0.5 given by the penetration model. Janssen and Van Stralen [36] have discussed the case where the log$K$/log V slope is higher than the prediction of the penetration model.

A possible approach to explain the relatively low log$K$/log V slope in the case of low discharge rates of small bubbles is to consider the case as a natural convection problem where mass is transferred to the surface by virtue of the buoyancy force arising from the density difference between the gas–liquid dispersion at the electrode surface and the bulk solution. At low gas discharge rate it is plausible to assume that the case corresponds to laminar flow natural convection. Mass transfer rates under such conditions are expressed by the equation [45]:

$$Sh = a(Sc \cdot GR)^{0.25} \tag{5}$$

where

$$Gr = \frac{gL^3}{\nu^2}\frac{\Delta\rho}{\rho}. \tag{6}$$

$\Delta\rho$ is the difference between the electrolyte bulk density, ρ_l, and the density of the gas–liquid dispersion at the electrode surface $\bar{\rho}$. The average density of the gas–liquid dispersion is given by:

$$\bar{\rho} = \rho_g\epsilon + (1-\epsilon)\rho_l \simeq (1-\epsilon)\rho_l \tag{7}$$

where the voidage ϵ is the fraction of the total volume occupied by the gas and ρ_g and ρ_l are the density of the gas and liquid, respectively, (the density of the gas being neglected as compared to that of the liquid, $\rho_g \ll \rho_l$). Substituting for $\bar{\rho}$ in equation [6]:

$$Gr = \frac{gL^3}{\nu^2}\frac{\rho_l-(1-\epsilon)\rho_l}{(1-\epsilon)\rho_l} \tag{8}$$

$$Gr = \frac{gL^3}{\nu^2}\frac{\epsilon}{1-\epsilon}. \tag{9}$$

At low gas discharge rates the void fraction ϵ can be neglected compared to 1, hence:

$$Gr = \frac{gL^3}{\nu^2}\epsilon. \tag{10}$$

Since

$$\epsilon = \frac{kV_g^n}{kV_g^n + V_l} \text{ with } n < 1. \tag{11}$$

At low gas discharge rates

$$(kV_g^N \ll V_l)\ [46], \qquad \epsilon = kV_g^n/V_l. \tag{12}$$

Therefore,

$$Gr = \frac{gL^3}{\nu^2}\frac{V_g^n}{V_l}. \tag{13}$$

Substituting Equation 13 in Equation 5,

$$Sh = a\left(Sc\frac{gL^3kV_g^n}{\nu^2V_l}\right)^{0.25}. \tag{14}$$

This can be put in the form

$$K = \bar{a}D^{0.75}\left(\frac{V_g^n}{Lv^2V_l}\right)^{0.25}. \qquad (15)$$

From Equation 15 it is seen that the $\log k/\log V_g$ slope is less than 0.25. This is consistent with the value of 0.19 obtained in the present work, and also agrees with the value obtained by Fouad and Sedahmed [39] for a H_2 evolving horizontal cylinder in alkaline solution (0.239). Polyakov *et al.* [43] studied the effect of carbon dioxide gas formed by the discharge of O^{2-} ion at a graphite electrode from a molten bath on the rate of mass transfer of O^{2-} ions to the anode and found that the $\log K/\log V$ slope was 0.24 agreeing with the prediction of the present model. Sedahmed *et al.* [40, 41] reported values for $\log K/\log V$ slope of 0.21 and 0.233 in the anodic dissolution of copper plates and cylinders in H_3PO_4 under oxygen evolving conditions.

As in single phase natural convection, if the buoyancy force increases sufficiently, e.g. at higher gas discharge rates, the flow may become turbulent. Recently Janssen and Barendrecht [35] dealt with this case in a similar manner to account for a slope of 0.33 obtained by him at a H_2 evolving electrode using alkaline solution where no H_2 bubble coalescence takes place. A similar approach was also used by Zuber [46] to account for his nucleate boiling heat transfer results. However, much work remains to be done in order to define more clearly the criteria and conditions under which different models can be applied to gas evolving electrodes.

Figure 2 shows that electrode position (vertical or horizontal) has no effect on the mass transfer coefficient. Studies on flat electrodes [34, 38] have shown that for the same rate of gas discharge (O_2 or H_2) the mass transfer coefficient at horizontal electrodes is slightly higher than that at vertical electrodes. At O_2 evolving screens the insensitivity to electrode position is consistent with the penetration mechanism which is independent of electrode position. However with H_2 evolving screens which involve the macroconvective mass transfer mechanism as shown by the present model, the two positions may be expected, within the range of experimental error, to give similar mass transfer coefficients under identical hydrodynamic conditions and electrode dimensions. This expectation is based on the fact that the equations representing single phase laminar natural convection mass transfer at horizontal and vertical electrodes are almost similar [45].

Figures 3 and 4 show the effect of the number of screens per bed on the mass transfer coefficient. In the case of H_2 evolving electrodes, the mass transfer coefficient increases slightly with an increase in the number of screens while in the case of O_2 the reverse is true. Again the difference in behaviour between O_2 and H_2 evolving electrodes can be ascribed to the difference in bubble size

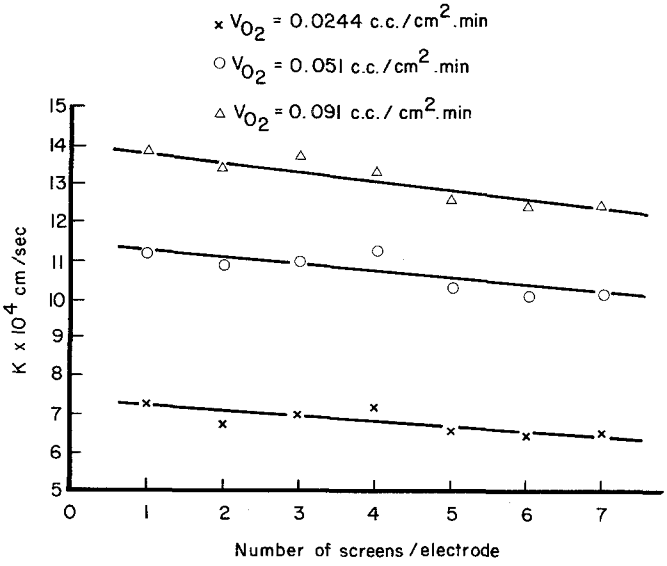

Fig. 3. Effect on the number of screens per electrode on the mass transfer coefficient at O_2 evolving electrode.

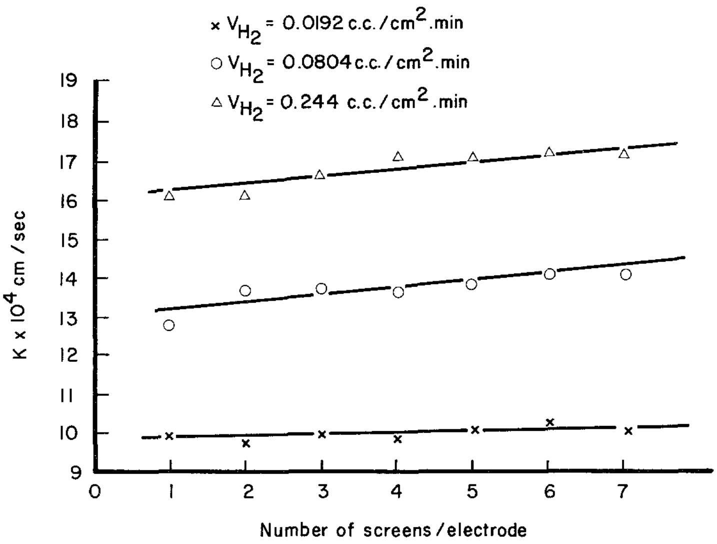

Fig. 4. Effect of the number of screens per electrode on the mass transfer coefficient at H_2 evolving electrode.

and the tendency of these bubbles to coalesce [27]. The detachment and movement of the large O_2 bubbles inside the bed is hindered by the matrix structure, while the small-sized H_2 bubbles find their way more easily through the matrix and enhance the rate of mass transfer as they move upward through the electrode.

To test the economic feasibility of using packed

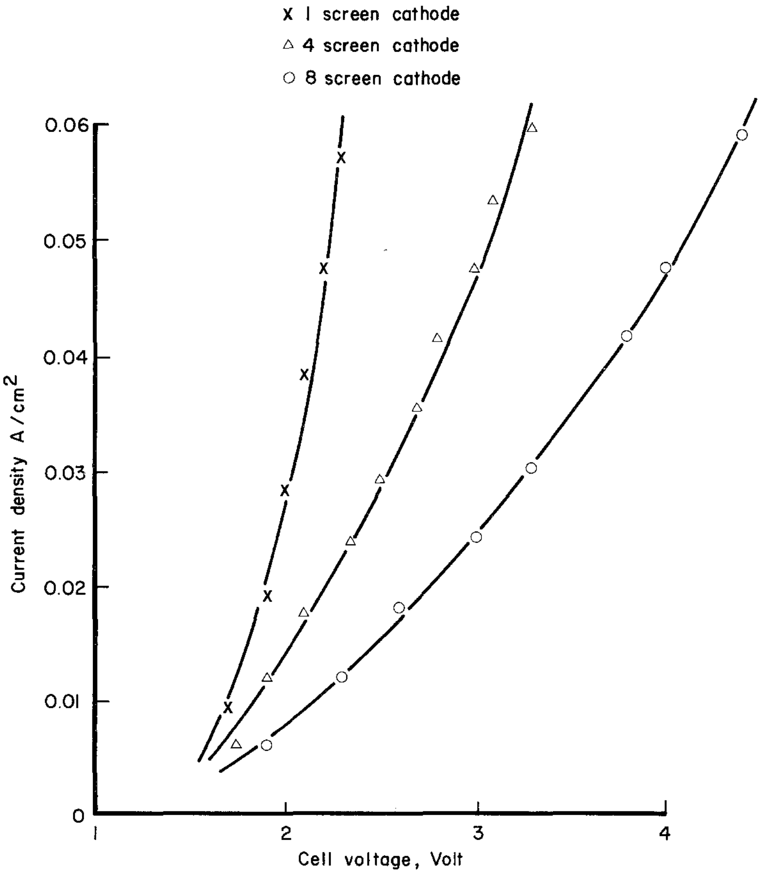

Fig. 5. Polarization at H_2 evolving screen electrodes.

Table 1. Effect of cell current on power consumption for the cathodic reduction of $K_3Fe(CN)_6$ at 4 screen packed bed H_2 evolving electrode; $C = 0.1$ M and $t = 26$° C

Total cell current (A)	*Cell voltage* (V)	*K* (cm s^{-1})	*% Current efficiency*	*Power Consumption* (kWh kg^{-1})
1	2.3	0.00089	72.0	0.260
2	2.7	0.001368	55.5	0.396
3	3.3	0.001628	44.0	0.610
4	3.8	0.001725	35.0	0.884
5	4.2	0.001959	31.8	1.081
6	4.6	0.002026	27.4	1.368
7	5.0	0.002149	24.9	1.635

bed electrodes for conducting diffusion controlled reactions accompanied by gas evolution, polarization was measured for both H_2 evolving single and multiscreen electrodes as shown in Fig. 5. Polarization increases with increasing the number of screens per bed. Table 1 summarizes energy consumption calculations at different operating currents for the cathodic reduction of $K_4Fe(CN)_6$ at a H_2 evolving bed electrode (4 screens). Table 1 shows that the beneficial effect of H_2 evolution on the rate of mass transfer is outweighed by the increase in voltage drop and power consumption of the cell.

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References

[1] A. A. Wragg and L. L. R. Whiteley, Extended Abstracts, 32nd Meeting of SIE, Dubrovnik, Yugoslavia, September 1981, p. 1106, V.II.
[2] C. L. Lopez-Cacicedo, *Trans. Inst. Met. Finishing* **53** (1975) 74.
[3] *Idem, Inst. Chem. Eng. Symp. Ser. No.* **42** (1975) 29.
[4] *Idem,* Proceedings of the Symposium on Less Common Uses of Electricity in the Process Industries, Institution of Chemical Engineers, July (1979).
[5] C. Chou and J. C. Chang, *Chem. Eng. Sci.* **35** (1980) 1581.
[6] B. Surfleet and V. A. Crowle, *Trans. Inst. Met. Finishing* **50** (1972) 227.
[7] L. W. Shemilt and G. H. Sedahmed, *J. Appl. Electrochem.* **6** (1976) 471.
[8] G. H. Sedahmed and L. W. Shemilt, to be published.
[9] A. A. Wragg, *Int. J. Heat Mass Transfer* **11** (1968) 979.
[10] G. H. Sedahmed, *J. Appl. Electrochem.* 8 (1978) 399.
[11] R. Alkire and B. Gracon, *J. Electrochem. Soc.* **122** (1975) 1594.
[12] R. E. Sioda, *Electrochim. Acta* **15** (1970) 783.
[13] *Idem, ibid.* **17** (1972) 1939.
[14] *Idem, ibid.* **22** (1977) 439.
[15] R. E. Sioda, *J. Appl. Electrochem.* 7 (1977) 135.
[16] *Idem, J. Electroanal. Chem.* **34** (1972) 411.
[17] A. Storck, P. M. Robertson and N. Ibl, *Electrochim. Acta* **24** (1979) 373.
[18] J. Cano and U. Böhm, *Chem. Eng. Sci.* **32** (1977) 213.
[19] M. A. Shah and D. Roberts, 'Advances in Chemistry, Series 133 – Chemical Reaction Engineering II (1974).
[20] B. Gay and R. Maugham, *Int. J. Heat Mass Transfer* **6** (1963) 277.
[21] C. N. Satterfield and D. H. Cortez, *Ind. Eng. Chem Fundamentals* **9** (1970) 613.
[22] P. H. Vogtlander and C. A. P. Bakker, *Chem. Eng. Sci.* **18** (1963) 583.
[23] E. Sutzkover, C. Zur and M. Ariel, *Israel J. Chem.* **18** (1979) 99.
[24] W. J. Blaedel and S. L. Boyer, *Anal. Chem.* **45** (1973) 258.
[25] M. G. Fouad and G. H. Sedahmed, *Electrochim. Acta* **20** (1975) 615.
[26] N. Ibl, R. Kind and E. Adam, *An. Quim.* **71** (1975) 1008.
[27] L. J. J. Janssen and J. G. Hoogland, *Electrochim. Acta* **18** (1973) 543.
[28] *Idem, ibid.* **15** (1970) 1012.
[29] N. Ibl and J. Venczel, *Metalloberfläche* **24** (1970) 365.
[30] H. Vogt, PhD thesis, Stuttgart (1977).
[31] A. I. Vogel, 'A Textbook of Quantitative Analysis', 2nd edn., Longmans (1960).
[32] J. C. Armour and J. N. Cannon, *AIChE J.* **14** (1968) 415.
[33] R. Alkire and P. Y. Lu, *J. Electrochem. Soc.* **126** (1979) 2118.
[34] L. J. J. Janssen, *Electrochim. Acta* **23** (1978) 81.
[35] L. J. J. Janssen and E. Barendrecht, *ibid.* **24** (1979) 693.
[36] L. J. J. Janssen and S. J. D. Van Stralen, *ibid.* **26** (1981) 1011.

[37] M. G. Fouad and G. H. Sedahmed, *ibid.* **17** (1972) 665.
[38] *Idem, ibid.* **18** (1973) 55.
[39] *Idem, ibid.* **19** (1974) 861.
[40] G. H. Sedahmed, I. A. S. Mansour, A. A. Zatout and N. A. Abdel-Hay, *J. Appl. Electrochem.* **10** (1980) 543.
[41] G. H. Sedahmed, A. A. Zatout, I. A. S. Mansour and N. A. Abdel-Hay, *Surf. Technol.* **11** (1980) 61.
[42] J. Rousar and V. Cezner, *Electrochim. Acta* **20** (1975) 289.
[43] P. V. Polyakov, V. M. Shestakov, V. V. Burnakin and Y. M. Ryabukhin, *Electrokhimya* **16** (1980) 685.
[44] F. O. Mixon, W. Y. Chou and K. O. Beatty, *Heat Transfer* **56** (1960) 75.
[45] J. R. Selman and C. W. Tobias, *Advan. Chem. Eng.* **10** (1978) 211.
[46 N. Zuber, *Int. J. Heat Mass Transfer* **6** (1963) 53.