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Criterion of completeness of electrolysis at flow porous electrodes

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An equation is presented which allows the calculation of the critical solution flow velocity corresponding to complete reaction controlled by diffusion at flow porous electrodes. The equation has been experimentally confirmed with good accuracy for the mass transport-controlled reaction of the reduction of $K_3Fe(CN)_6$ at flow porous electrodes composed of fine platinum screens and of gilded graphite granules described in the literature. If the critical flow velocity can be determined experimentally, the equation may be used for the determination of the specific surface of the electrode or the diffusion coefficient of the process. In this way the specific surfaces of graphite electrodes have been determined, which also enabled the calculation of mass transfer coefficients and dimensionless correlations for the Sherwood Number and j_D-factor.

List of symbols

A'	Empirical constant in Equation 5
B	Empirical constant in Equation 5
d_p	Particle diameter (cm)
D	Diffusion coefficient ($cm^2 s^{-1}$)
j_D	j_D-factor, $j_D = (Sh)(Re)^{-1}(Sc)^{-1/3}$
k	Coefficient of mass transfer ($cm\,s^{-1}$)
L	Electrode height (cm)
M	$\log_{10}e = 0{\cdot}4343$
r	Pore radius (cm)
r_1	Coefficient of correlation
R	Limiting degree of conversion
R_c	Critical limiting degree of conversion
$\bar{R}_c$	Average critical limiting degree of conversion
(Re)	Reynolds Number, $(Re) = ud_p/\nu$
R_h	Hydraulic radius (cm)
s	Specific surface (cm^{-1})
(Sc)	Schmidt Number, $(Sc) = \nu/D$
$(\overline{Sc})$	Average Schmidt Number
(Sh)	Sherwood Number, $(Sh) = kd_p/D$
T	Absolute temperature (K)
u	Superficial flow velocity ($cm\,s^{-1}$)
u_c	Critical superficial flow velocity ($cm\,s^{-1}$)
w	Interstitial flow velocity ($cm\,s^{-1}$)
ϵ	Void fraction
η	Dynamic viscosity (poise)
Φ	Dimensionless parameter
ν	Kinematic viscosity ($cm^2 s^{-1}$)

1. Introduction

Although flow porous electrodes have only been investigated since 1957 [1], they have already found important applications. In 1972 Bennion and Newman described a laboratory flow electrolytic cell with electrodes composed of carbon flakes, which served for the purification of water from heavy metal impurities, especially copper. Employing this cell it was possible to reduce the copper content of the solution from an initial value of approximately 670 mg l^{-1} to less than 1 mg l^{-1} [2]. The idea of the application of flow porous electrodes for the deposition of heavy metals from dilute solutions has been further developed both in the laboratory and on a pilot plant scale. Wenger and Bennion described an improved cell for recovering copper from dilute solutions [3]. Carlson constructed an industrial cell with a graphite porous cathode for the purification of brine and sodium hydroxide solutions from mercury and other heavy metals [4, 5]. Williams and co-workers at Du Pont constructed a 100 gal min^{-1} pilot plant installation with a stainless steel mesh cathode for recovering Hg, Ag, Au, Pb and Cu from diluted process wastes [6–8]. Kennecott Copper Corporation has recently developed a process employing a flow electrolytic cell with porous cathodes prepared of coke slurry for retrieving residual copper from dilute leach liquors in copper hydrometallurgy. According to preliminary field results the process is economically competitive with non-electrochemical methods [9].

An important practical problem is the optimization of flow porous electrodes. It is evident that the maximal utilization of flow porous electrodes is connected with their operation in the diffusion regime, when the total rate of electrolysis is limited by the rate of mass transport to the internal surface of the electrode. The rate of mass transport may be calculated with the help of the traditional engineering methods based on dimensionless correlations. Another important practical problem is the calculation of the minimal residence time of a solution in the electrode necessary for achieving a complete transformation of the dissolved substance, i.e. for obtaining a degree of conversion practically equal to unity. This problem has been treated by Kenkel and Bard [10], and recently also by Ateya [11, 12]. The adopted approach is based on the Einstein–Smoluchowski equation for the average rate of diffusion [13]. In the present paper this concept is further generalized and applied to the earlier published experimental results obtained with flow porous electrodes composed of fine screens [14], and of graphite granules [15, 16].

2. Theory

Kenkel and Bard calculated the maximal solution flow-rate through a given porous electrode leading to the practically complete transformation of a dissolved substance. For this purpose they compared the average time of diffusion of the substance in the pores with the time of residence of the solution in the electrode. When the time of diffusion was shorter than the residence time, the complete transformation of the substance was expected. Mathematically the postulate of Kenkel and Bard takes the form of the following inequality for the case of the exhaustive electrolysis of substance [10]:

$$w \leqslant 2LD/r^2. \tag{1}$$

where w is the interstitial flow velocity in the pores, L the electrode length, D the diffusion coefficient, and r the radius of pores in the electrode. A similar approach to the problem was adopted by Ateya [11, 12], who introduced a dimensionless parameter Φ equal to the ratio of the diffusion time in the pores to the residence time of solution in the electrode:

$$\Phi = \frac{wr^2}{2DL}. \tag{2}$$

The complete substance conversion is possible for $\Phi \leqslant 1$, for $\Phi > 1$ the substance reacts in the electrode only partially.

Inequality 1 and Equation 2 can be applied for electrodes of such a structure that a medium pore radius may be easily determined. For electrodes having a less ordered structure, by analogy with packed beds and columns [17], the medium pore radius may be substituted by two hydraulic radii, $r = 2R_{\text{h}}$, where

$$R_{\text{h}} = \frac{\epsilon}{s}. \tag{3}$$

ϵ is the void fraction, and s the specific surface of the electrode. Instead of the interstitial flow velocity w it is convenient to use a superficial flow velocity $u = w\epsilon$, which is the ratio of the volume flow-rate and the flow cross-section area. It is also useful to define a critical superficial flow velocity, u_{c}, such that the pore diffusion time is equal to the residence time. Then instead of Inequality 1 the following equation results:

$$u_{\text{c}} = \frac{LDs^2}{2\epsilon}. \tag{4}$$

For superficial flow velocities equal to or smaller than u_{c} complete electrolysis of the substance may be expected. Equation 4 has a significant practical value. It contains usually easily determinable quantities describing the electrode and the process (D). If, for a given process, u_{c} can be determined experimentally, from Equation 4 other quantities can be calculated, e.g. D or especially s. The value of Equation 4 consists also in the fact that it is general and should thus be applicable to packed beds and columns for predicting the conditions of complete reaction of processes controlled by mass transport.

3. Results

In the following discussion the experimental results described earlier [14, 15] are used to confirm the validity of Equation 4. Sioda investigated flow porous electrodes composed of parallel platinum screens by measuring the dependence of the limiting current on the solution flow-rate. From the

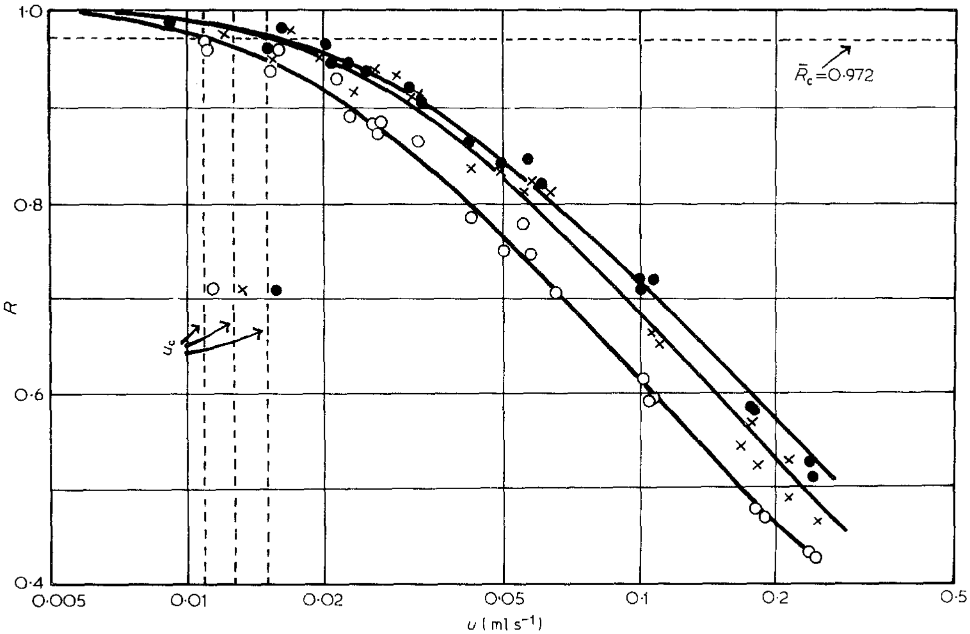

Fig. 1. The dependence of the limiting degree of conversion (R) on the solution superficial flow velocity (u) for the reduction of $2{\cdot}0 \times 10^{-3}$ M $K_3Fe(CN)_6$ in 1 M KCl in water at flow porous electrodes composed of 12 (○), 14 (×), and 16 (●) parallel platinum 80-mesh screens given after [14].

values of the limiting current the limiting degrees of conversion of substance were calculated and their dependence on solution flow-rate was established. Some of the experimental results obtained are shown in Fig. 1. In the figure the values of the critical superficial flow velocities calculated according to Equation 4 for the parameters of the electrodes and for the diffusion coefficient of the process $D = 0{\cdot}67 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ are also shown. The substitution of the obtained values of u_c in the determined functional dependence of the limiting degree of conversion on solution superficial flow velocity leads to the values of the limiting degree of conversion (called further the critical limiting degree of conversion and denoted R_c) shown in Table 1. The determined values of the critical limiting degrees of conversion are very close to unity, and thus confirm the validity of Equation 4.

A similar analysis can be performed with the data published by Coeuret [15] for the flow porous electrodes composed of gilded spherical graphite particles. Some of the results of Fig. 2 of the Coeuret's paper are presented in Fig. 2. The data have been recalculated in the form of the functional dependence of log log $[1/(1-R)]$ versus log u:

$$\log\log[1/(1-R)] = A' + B\log u \quad (5)$$

where R is the measured limiting degree of conversion, and A' and B are empirical constants. The values of the constants and of the coefficient of correlation r_1 shown in Table 2 have been obtained by the least squares method.

Using Equation 4 the critical superficial flow velocities, u_c, can be calculated for the parameters of the electrodes and for $D = 0{\cdot}60 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ given in the paper by Coeuret. The resulting u_c are

Table 1

Electrode	u_c (cm s^{-1})	R_c
12 screens	0·0109	0·975
14 screens	0·0127	0·981
16 screens	0·0150	0·973

Table 2

Electrode height (cm)	A'	B	r_1
1·0	−1·029	−0·652	0·998
1·5	−0·884	−0·592	0·997
2·0	−0·714	−0·586	0·997

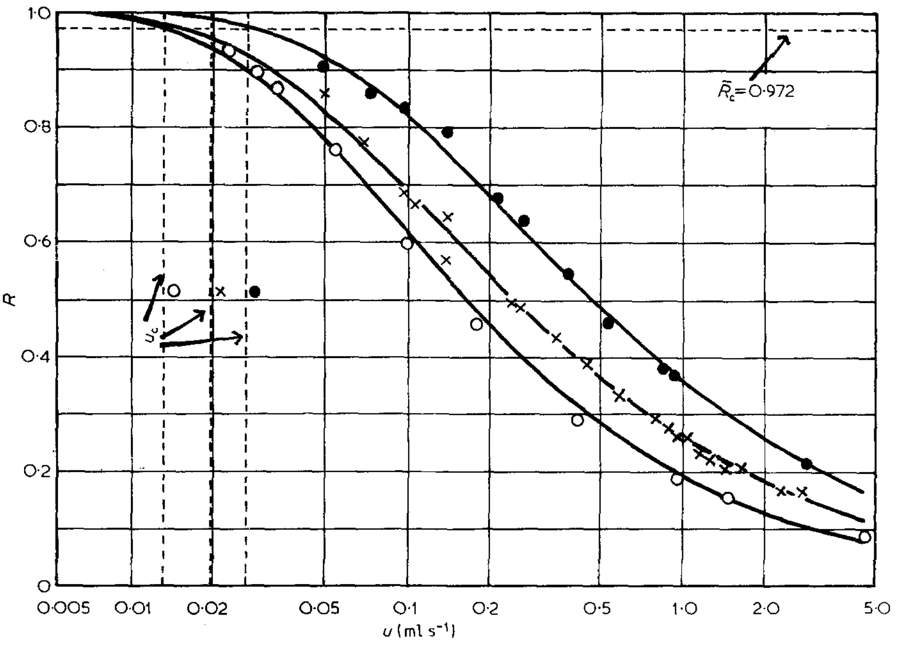

Fig. 2. The dependence of the limiting degree of conversion (R) on the solution superficial flow velocity (u) for the reduction of 1.0×10^{-3} M $K_3Fe(CN)_6$ in 1 M NaOH in water at flow porous electrodes composed of gilded graphite spheres of $d_p = 0{\cdot}085$ cm forming electrodes of the heights: $L = 1$ cm (o), 1·5 cm (×), and 2 cm (•) given after [15].

shown in Table 3 together with the critical limiting degrees of conversion calculated according to the determined functional dependence of R versus u.

The critical limiting degrees of conversion for the three screen electrodes and the three graphite electrodes are remarkably similar. The arithmetical average of the six determined R_c values is $\bar{R}_c = 0{\cdot}972$ with a standard deviation of 0·4%. The similarity of R_c for such different electrodes composed of screens and of spheres, and their closeness to unity confirms the validity of Equation 4 for flow porous electrodes of various structures.

The accuracy with which Equation 4 is fulfilled also supports the idea of applying the equation to the determination of unknown parameters, such as the diffusion coefficient or the specific surface, if the experimental dependence of the limiting degree of conversion on the solution superficial flow velocity was measured. This especially concerns the specific surface, which sometimes is difficult to determine, and remains unknown.

Table 3

Electrode height (cm)	u_c (cm s^{-1})	R_c
1·0	0·0132	0·973
1·5	0·0197	0·954
2·0	0·0263	0·977

For example, the present author studied electrodes composed of graphite granules of three mesh sizes and of irregular structure [16]. The photograph of the enlarged granules is given in Fig. 3. For the electrodes the dependence of the limiting degree of conversion on solution flow-rate was measured. However the mass transfer coefficient and the mass transfer correlations were not determined, because the specific surface of the electrodes was unknown. The specific surface can presently be estimated using Equation 4, after determining u_c from the functional dependence of R versus u as being the superficial flow velocity for which 97% of the substrate reacts. The value of 97% of reaction may seem somewhat arbitrary. However, it is supported by the results obtained for the platinum screen and gilded graphite electrodes described above. For these electrodes, R_c was strikingly close to 0·97 (standard deviation 0·4%). Besides, a small variation of R_c of the order of 2%, $0{\cdot}99 \geqslant R_c \geqslant 0{\cdot}95$, does not have a great influence on the value of u_c. Determined in this way, u_c, substituted into Equation 6, together

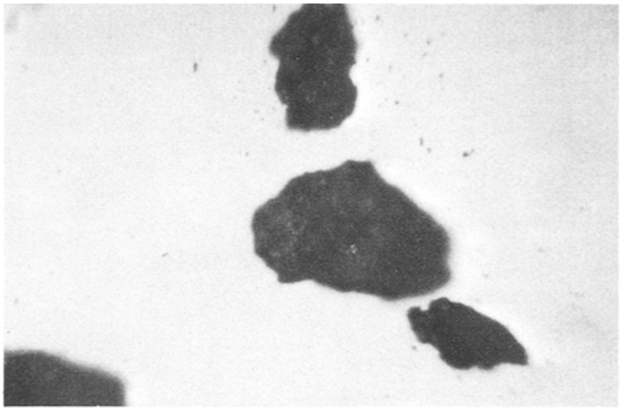

Fig. 3. Photograph of the graphite granules composing the flow porous electrodes described in [16].

with the respective values of D, ϵ and L will give the approximate values of the specific surface of the electrodes:

$$s = \sqrt{\left(\frac{2\epsilon u_c}{DL}\right)}. \qquad (6)$$

Thus using the data of [16], namely the dependence of log log[1/(1 − R)] versus the logarithm of the flow-rate averaged by means of the least-squares method, the values of u_c (for $R_c = 0{\cdot}97$) are obtained. They are shown in Figs. 4 and 5, and listed in Table 4, together with the values of the

Table 4

Electrode	u_c (cm s^{-1})	D (cm^{2}s^{-1})	s (cm^{-1})
I	0·0094	6·5 × 10^{-6}	56
II	0·0128	6·9 × 10^{-6}	52
III	0·0178	7·3 × 10^{-6}	53
IV	0·0212	6·8 × 10^{-6}	82
V	0·0382	6·2 × 10^{-6}	94
VI	0·0695	6·2 × 10^{-6}	155

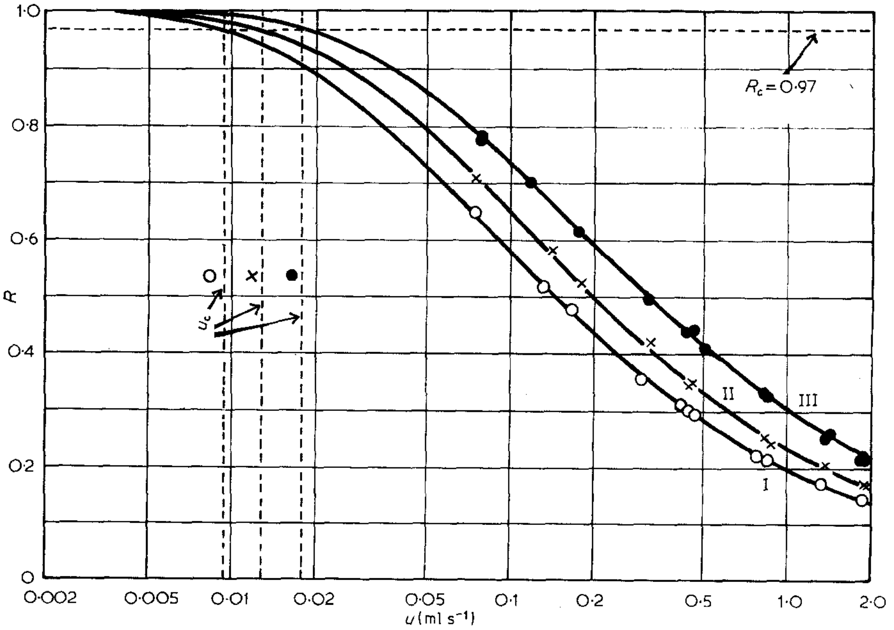

Fig. 4. The dependence of the limiting degree of conversion (R) on the solution superficial flow velocity (u) for the reduction of 2·0 × 10^{-3}M $K_3Fe(CN)_6$ in 2 M KCl in water at flow porous electrodes composed of irregular graphite granules given after [16]. Parameters of the electrodes: d_p = 0·068 cm, electrode height L = 0·57 cm (I), 0·85 cm (II), and 1·07 cm (III).

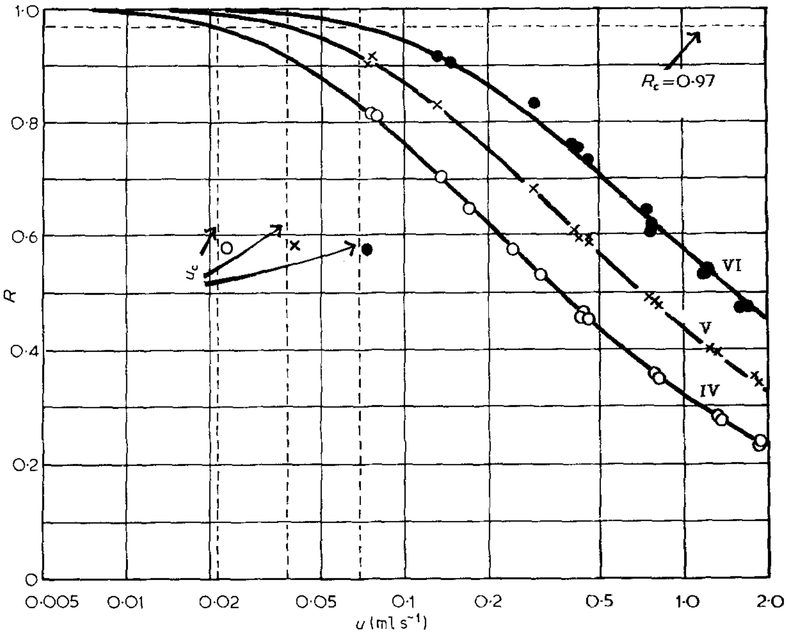

Fig. 5. The dependence of the limiting degree of conversion (R) on the solution superficial flow velocity (u) for the reduction of $2{\cdot}0 \times 10^{-3}$ M $K_3Fe(CN)_6$ in 2 M KCl in water at flow porous electrodes composed of irregular graphite granules given after [16]. Parameters of the electrodes: $d_p = 0{\cdot}044$ cm (IV and V), 0·024 cm (VI), electrode height $L = 0{\cdot}57$ cm (IV and VI), 0·85 cm (V).

diffusion coefficients and the values of the specific surfaces of the electrodes calculated by means of Equation 6. The diffusion coefficients were calculated by means of the Stokes–Einstein relation $D\eta T^{-1} = 2{\cdot}15 \times 10^{-10}\,\mathrm{cm^2\,poise\,s^{-1}\,K^{-1}}$ as given in [14]. The temperatures and consequently the viscosities of the solutions differed in separate experiments giving rise to the differences of the diffusion coefficients shown in Table 4. The viscosities of the investigated basic electrolyte solutions of 2 M KCl in water were calculated according to [18], assuming their temperature dependence to be similar to that of water.

Curves I and III in Fig. 4 were obtained for graphite granules of medium equivalent diameter of 0·068 cm; in Fig. 5 Curves IV and V were obtained for graphite granules of medium equivalent diameter of 0·044 cm, and Curve VI for graphite granules of medium equivalent diameter of 0·024 cm. As the granules formed electrodes of the same void fraction $\epsilon = 0{\cdot}61$, the specific surfaces of the electrodes should form a ratio equal to the ratio of the reciprocals of the medium equivalent diameters: 1:1·55:2·83. This ratio is compared with the ratio of the average determined specific surface: 53·7:88:155 = 1:1·64:2·89. The two independently obtained ratios agree well.

Knowing the specific surfaces of the electrodes, and the dependence of the limiting degree of conversion on the superficial flow velocity of the solution, the coefficient of mass transfer k can be calculated from the equation [19]:

$$\log k = A' - \log(MsL) + (1 + B)\log u \qquad (7)$$

where M is $\log_{10}e = 0{\cdot}4343$ and the constants A' and B are determined experimentally according to Equation 5. The values of the constants A' and B together with the calculated values of the mass transfer coefficients for the graphite electrodes [16] are given in Table 5.

Table 5

Electrode	A'	B	k
I	−1·012	−0·589	$0{\cdot}007\,u^{0{\cdot}41}$
II	−0·927	−0·587	$0{\cdot}0062\,u^{0{\cdot}41}$
III	−0·802	−0·563	$0{\cdot}0065\,u^{0{\cdot}44}$
IV	−0·771	−0·570	$0{\cdot}0084\,u^{0{\cdot}43}$
V	−0·597	−0·550	$0{\cdot}0073\,u^{0{\cdot}45}$
VI	−0·424	−0·524	$0{\cdot}0098\,u^{0{\cdot}48}$

Table 6

Electrode	(Sh)	j_D	(Sc)
I	$32(Re)^{0{\cdot}41}$	$2{\cdot}9(Re)^{-0{\cdot}59}$	1370
II	$26(Re)^{0{\cdot}41}$	$2{\cdot}4(Re)^{-0{\cdot}59}$	1230
III	$24(Re)^{0{\cdot}44}$	$2{\cdot}3(Re)^{-0{\cdot}56}$	1100
IV	$27(Re)^{0{\cdot}43}$	$2{\cdot}5(Re)^{-0{\cdot}57}$	1270
V	$26(Re)^{0{\cdot}45}$	$2{\cdot}3(Re)^{-0{\cdot}55}$	1490
VI	$24(Re)^{0{\cdot}48}$	$2{\cdot}1(Re)^{-0{\cdot}52}$	1500
average	$26{\cdot}5(Re)^{0{\cdot}44}$	$2{\cdot}4(Re)^{-0{\cdot}56}$	1330

From the mass transfer coefficients it is possible to calculate the dimensionless correlations for the Sherwood Number and j_D-factor:

$$(Sh) = kd_p/D \tag{8}$$

and

$$j_D = (Sh)(Re)^{-1}(Sc)^{-1/3} \tag{9}$$

where the dimensionless Reynolds Number and Schmidt Number are defined in the following way:

$$(Re) = ud_p/\nu \tag{10}$$

and

$$(Sc) = \nu/D \tag{11}$$

d_p being the particle diameter and ν the kinematic viscosity of the solution. The obtained correlations together with the corresponding values of the Schmidt Numbers are given in Table 6. The obtained Sherwood Numbers and j_D-factors diminish with increasing height of the electrode and with decreasing particle size. This probably can be explained by the effect of increasing contact resistance between particles, when the electrode height is increased, or when smaller particles are used. Consequently more of the particles become electrochemically inactive in a higher electrode, or electrode composed of smaller particles.

The obtained dimensionless correlations can be compared with the j_D-correlation of Wilson and Geankoplis [20] for the mass transfer to a packed bed of spherical particles. The authors found the following correlation at small Reynolds Numbers; $(Re) < 55$: $j_D\epsilon = 1{\cdot}09(Re)^{-2/3}$. When the value of the void fraction, $\epsilon = 0{\cdot}61$, of the graphite electrodes is substituted, the following correlation is obtained: $j_D = 1{\cdot}79(Re)^{-2/3}$. The numerical factor in this correlation is substantially smaller than the respective factors of the j_D-correlations determined for the graphite electrodes. The reason for this discrepancy is unknown at present. Coeuret [15] obtained the following correlation for packed bed electrodes composed of gilded spherical graphite particles: $(Sh) = 5{\cdot}4(Re)^{1/3}(Sc)^{1/4}$. After substitution in this correlation of the above average value of the Schmidt Number $(\overline{Sc}) = 1330$ the following correlation is obtained: $(Sh) = 33(Re)^{1/3}$. The numerical factor in this correlation is higher than the average value of the factor obtained in the present work (26·5). This difference can be explained as being due to a better electrical contact in the electrodes of Coeuret caused by gilding of the graphite spheres. Consequently a higher percentage of the particles in the electrodes of Coeuret are active than in the case of the graphite electrodes of the present author. This conclusion is supported by the observation that in the electrode of small height and composed of the largest particles (Electrode I), where the contact resistance should be the lowest, the numerical factor is the highest (32) and practically equal to that in the corresponding Coeuret correlation (33).

4. Conclusions

The proposition of Kenkel and Bard [10] and also of Ateya and co-workers [11, 12] of estimating the conditions of a complete electrolysis at flow porous electrodes has been generalized by the introduction of the notion of hydraulic radius. The resulting equation, Equation 4, allows the calculation of the critical solution superficial flow velocity, which should lead to a complete or almost complete electrolysis of the flowing substance under conditions of mass transfer control of the reaction. The validity of Equation 4 has been checked using the earlier experimental results of the electrolysis at flow porous electrodes composed of parallel 80-mesh platinum screens [14] and of spherical gilded graphite granules [15]. It has been found that the calculated critical flow velocities for the electrodes corresponded to on average 97·2% completeness of the electrolysis of the flowing substance (standard deviation 0·4%). This result confirms the validity of the application of Equation 4 for predicting the conditions of a complete electrolysis at flow porous electrodes of various structures.

The accuracy with which Equation 4 has been fulfilled for the investigated electrodes indicates also a possibility of the application of this equation to a determination of the specific surface of a given flow porous electrode or the diffusion coefficient of the substance. For this purpose the critical superficial flow velocity has to be determined independently of Equation 4 from the measured dependence of the limiting degree of conversion on the superficial solution flow velocity. In this way the earlier experimental results of the electrolysis at flow porous electrodes composed of irregular graphite granules [16] have been presently used to determine the specific surface of the electrodes. The validity of the obtained values of the specific surface is confirmed, as they form a ratio in accordance with the ratio of reciprocals of the medium equivalent particle diameters. The determined values of the specific surface have been further used in the calculation of mass transfer coefficients and the dimensionless correlations for Sherwood Number and j_D-factor. The obtained correlation for the Sherwood Number agrees with the correlation determined by Coeuret for the electrodes composed of gilded spherical graphite particles [15].

It is believed that Equation 4 together with the transformed Equation 6 have a general significance, and should also apply to non-electrochemical packed beds and columns working in the diffusion regime.

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