

A model-based analysis of heat transport in electrolytic reactors

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Received 6 February 1985; revised 22 April 1985

Thermal behaviour and heat transport phenomena occurring in electrolytic reactors are analysed via the governing equations of appropriate models. Applications of the continuous-flow stirred tank electrochemical reactor (CSTER) and plug-flow electrochemical reactor (PFER) models to estimate temperature profiles in electrolyzers are discussed.

Nomenclature

a, b	regression parameters for $(\Delta H_w, T)$	n_k	mole fraction of the k th component
a_s	specific investment cost	N_k	substance flux of the k th ionic component
A_E	electrode area	P	pressure
A_j	the area of the j th heat transfer surface	P_w	vapour pressure of water at the evaporating surface
A_s	electrolyte surface area	P_∞	vapour pressure of the ambient water vapour
b_s	specific cost of electric energy	\mathbf{q}	heat flux vector
c	electrolyte concentration	Q_L	rate of heat losses
C_H	specific cost of thermal energy	R_e	electrolyte resistance
C_i	specific cost of thermal insulation	R_k	rate of homogeneous production in chemical reaction of the k th ionic species, per unit area
C_k	concentration of the k th ionic species	S	separation distance of electrolyser walls parallel to plug flow direction
c_0	solvent concentration	S_1, S_2	dimensions of the horizontal section of a rectangular electrolyser
C_p	specific heat of the electrolyte	T	temperature
c_T	total solution concentration	T_A	ambient temperature
C_T	composite cost	t	time
d_i	insulation thickness	U	overall heat transfer coefficient; U_j pertains to the j th heat transfer surface
\mathcal{D}	electrolyte diffusivity (based on a thermodynamic driving force)	V_i	insulation volume
D/Dt	substantive differential operator	v_k	velocity of the k th ionic component
F	Faraday's constant	\mathbf{V}	velocity vector
G	mass flow rate of electrolyte	w	electrode area per unit reactor length
\bar{H}_k	partial molar enthalpy of the k th ionic species	α_1	lumped parameter $(U/Sq c_p)$
h_s	surface-to-air heat transfer coefficient	α_2	lumped parameter $(i_m^2/qc_p\sigma_m)$
I	electric current	α_4, β_4	regression parameters for (σ, T)
i	electric current density	β_1	lumped parameter $(U/V_x Sq c_p)$
k_i	thermal conductivity of insulation	β_2	lumped parameter $(1/V_x q c_p)$
L	characteristic length		
\bar{m}	average rate of evaporation		
M	heat capacity of electrolyte mass in reactor		

β_3	lumped parameter ($\Delta H_R/V_x S \varrho c_p z F$)	σ	electrolyte conductivity
ΔH_R	heat of the overall electrolytic cell reaction	σ_s	Soret coefficient
ΔH_w	latent heat of vapourization (of water); $\Delta \hat{H}_w$ its estimated value by regression	τ	PFER time constant
ν	dissociation number (number of ion moles produced by the dissociation of one mole of electrolyte)	τ	stress tensor
ν_i	ionic dissociation number (number of moles of the k th ionic species produced by the dissociation of one mole of electrolyte)	ω_e	mass fraction of the electrolyte
ϱ	electrolyte density	<i>Subscripts</i>	
		m	average
		L	at exit site
		S	steady state
		x	along the principal direction of axial flow

1. Introduction

In many electrochemical reactors, the overall enthalpy flow due to the generation of Joule heat via electric current, physical flow of the electrolyte and the dissipation of thermal energy towards the surroundings results in relatively high operating temperatures (e.g. production of metals via molten salt electrolysis). From the viewpoint of energy availability analysis (exergy), the distribution of enthalpy flows is often far from optimal; thermal energy may be dissipated at high rates instead of conserving it for release in another portion of the plant. In an exergy-based economic analysis the enthalpy flow distribution pattern in an electrochemical reactor, especially in an electrolyser, has as important a function as the electrical energy itself. An analysis of thermal reactor performance may well indicate the desirability of thermal insulation on a reactor with an optimal thickness determined by relative energy cost/insulator cost indices. These aspects have not yet been explored in a thorough manner for the benefit of economy-conscious design of electrochemical reactors.

The purpose of this paper is to present a fundamental framework for the analysis of thermal characteristics of electrolytic reactors based on the concept of heat balances and elementary heat transport theory. It is shown that the electrochemical equivalents of the CSTR and PFR model, called CSTER and PFER, can be used advantageously in obtaining relatively simple analytical relationships to estimate, at least in an order-of-magnitude sense, steady-state temperatures, steady-state temperature profiles and transient temperatures. The discussion is focused primarily on electrolysers but it applies in principle to any electrochemical reactor.

2. The mathematical framework

Let \mathbf{N}_k be the vector field representing the flux of the k th ionic species in a bounded close region Ω of an electrolyte space. If S is a (piecewise) smooth surface forming a complete boundary of Ω , and \mathbf{n} is the outer normal of S with respect to Ω , then the classical divergence theory of Gauss (e.g. [1])

$$\iint_S \mathbf{N}_k \cdot \mathbf{n} dS = \iiint_{\Omega} \text{div } \mathbf{N}_k dV \quad (1)$$

provides the fundamental balance for an electrolyte contained in volume V . If the electrolyte is binary (i.e. $k = 1, 2$ representing one cationic and one anionic species of interest, respectively) then \mathbf{N}_1 and \mathbf{N}_2 can be expressed in terms of individual contributions of migrational, diffusional and convective fluxes, as shown by Newman [2]. The ionic flux carries a direct contribution of thermal origin,

$$\mathbf{N}_k^{(i)} = \frac{\nu_k \mathcal{D}_T c}{\nu} \frac{\omega_e \sigma_s}{(c_0 + c)} \text{grad } T \quad (2)$$

but there is also an indirect contribution of the vector field $\text{grad } T$ via the temperature dependence of physical parameters, e.g. electrolyte density, viscosity, diffusivity and ionic transference number. It follows immediately that temperature variations influence enthalpy-flow conditions (notably energy losses) *as well as* current distribution and mass transport conditions in an electrochemical reactor: mass and heat transport aspects cannot be separated in a meticulous analysis of electrochemical reactor performance. From a practical point of view, however, a rigorous treatment of material and heat balances would run into several difficulties. Firstly, the variation of the physical parameters is known only within a limited range of concentration and temperature; secondly, even if such variations were fully known, e.g. regression equations, the balance equation still could not be solved analytically and their numerical solution would be rather cumbersome. In a compromise approach to the problem, material and heat balances have to be decoupled and handled separately.

One possible starting point is a semi-rigorous thermal balance [2], rewritten slightly [3] as

$$\rho c_p \frac{DT}{Dt} + \left(\frac{\partial \ln \rho}{\partial \ln T} \right)_{P,n_k} \frac{DP}{Dt} = -\text{div } \mathbf{q} - \tau : \text{div } \mathbf{v} + \sum_k \bar{H}_k (\text{div } \mathbf{J}_k - R_k) \quad (3)$$

$$\mathbf{J}_k \equiv \mathbf{N}_k - c_k \mathbf{v}$$

neglecting the temperature dependence of density and specific heat capacity, except in the substantive pressure derivative term. The terms of the right hand side of Equation 3 express the contribution of enthalpy flux, thermal flux generated by viscous dissipation and heat generated or consumed by the electrode processes and chemical reactions (of non-electrochemical nature), respectively. In this formulation the $\sum \bar{H}_k \text{div } \mathbf{J}_k$ component includes the Joule effect, an important source of thermal energy in many electrolytic (especially fused salt) processes. If Equation 3 were to be solved rigorously, a large number of boundary conditions for T , P , \mathbf{q} and \mathbf{v} , not usually available, would have to be known. To simplify matters, pressure variations and viscous dissipation may be neglected; if the contribution of purely chemical reactions is negligible and if the thermal effects of the electrode processes are much smaller than Joule heat generation, the degenerate form of Equation 3 may be written as

$$\rho c_p \frac{DT}{Dt} \cong -\text{div } \mathbf{q} + \frac{|\mathbf{i}|^2}{\sigma} \quad (4)$$

where \mathbf{q} includes, of course, heat flux losses as well as enthalpy transfer via electrolyte flow into and out of the reactor. Under steady-state conditions ($\partial T/\partial t = 0$),

$$\mathbf{v} \cdot \text{grad } T_s \cong -\frac{1}{\rho c_p} \text{div } \mathbf{q}_s + \frac{|\mathbf{i}_s|^2}{\rho c_p \sigma} \quad (5)$$

represents the spatial distribution of temperature in an electrochemical system. In spite of its deceptively simple appearance (at least from a mathematical point of view) the solution of Equations 4 or 5 is by no means trivial and analysis requires further simplification via reduced models. The CSTER model and the PFER model will be used extensively in the sequel for this purpose.

3. Analysis of thermal behaviour via CSTER model

The CSTER is a variation of the theme of a CSTR, well known in the theory of chemical reaction engineering, taking specific aspects (such as the flow of electric current) of electrochemical systems into account. Thus, all spatial variations of temperature are neglected and all physical parameters are considered to be constants. Equation 4 is accordingly simplified, with the exception of retaining the thermal effect of the electrode reactions, in order to obtain the balance equation [4]

$$M \frac{dT}{dt} = Gc_p(T_i - T) + I^2R_e - \frac{I\Delta H_R}{zF} - Q_L \quad (6)$$

For the sake of a convenient calculation of the heat losses the terms in Equation 6 express energy flow rather than energy flux. The steady-state heat balance

$$I_s^2R_{e,s} = Gc_p(T_s - T_{i,s}) + \frac{I_s\Delta H_R}{zF} + Q_{L,s} \quad (7)$$

may be used for computing the steady-state reactor temperature T_s . Further simplifications may be made in the following instances.

(a) Heat colouration of electrode processes negligible:

$$M \frac{dT}{dt} = Gc_p(T_i - T) + I^2R_e - Q_L \quad (8a)$$

$$I_s^2R_{e,s} = Gc_p(T_s - T_{i,s}) + Q_{L,s} \quad (8b)$$

(b) Batch electrochemical reactor:

$$M \frac{dT}{dt} = I^2R_e - \frac{I\Delta H_R}{zF} - Q_L \quad (9a)$$

$$I_s^2R_{e,s} = \frac{I_s\Delta H_R}{zF} + Q_{L,s} \quad (9b)$$

(c) Well-insulated batch electrochemical reactor:

$$M \frac{dT}{dt} \cong I^2R_e - \frac{I\Delta H_R}{zF} \quad (10a)$$

$$I_s^2R_{e,s} \cong \frac{I_s\Delta H_R}{zF} \quad (\text{where } \Delta H_R > 0) \quad (10b)$$

In order to estimate transient temperature profiles, Equation 6 may be regarded either as a differential equation or as a definite integral with a varying upper limit. The latter interpretation is particularly attractive if the electrochemical reactions proceed under constant current (galvanostatic) conditions. Assuming an average heat-sink (ambient) temperature \bar{T}_A for heat losses and an overall thermal conductance $K_0 = \sum_{j=1}^N U_j A_j$, the heat loss rate may be written simply as $Q_L = K_0(T - \bar{T}_A)$ and Equation 6 is rearranged to

$$t = M \int_{T_0}^T \frac{dT}{G(T_i - T) - K_0(T - \bar{T}_A) + K_1} \quad (11)$$

$$K_1 \equiv I^2R_e - \frac{I\Delta H_R}{zF}$$

If R_e and ΔH_R do not vary appreciably with temperature, then $K_1 = \text{constant}$ and Equation 11 may be integrated via elementary calculus to yield the transient temperature profile

$$T = T_0 \exp\left(-\frac{G + K_0}{M} t\right) + \frac{GT_i + K_0\bar{T}_A + K_1}{G + K_0} \left[1 - \exp\left(-\frac{G + K_0}{M} t\right)\right] \quad (12a)$$

in the reactor. It is interesting to note that the apparent reactor time constant, $M/(G + K_0)$ is independent of the electric current, whereas the steady-state temperature

$$T_s = \frac{GT_i + K_0\bar{T}_A + K_1}{G + K_0} \quad (12b)$$

is quadratically related to it, according to the simplified CSTER model.

4. Analysis of thermal behaviour via PFER model

An electrochemical reactor operating under plug-flow conditions may be described via the PFER model sketched in Fig. 1. Since electrolyte flow in all but the axial direction is neglected, the substantive derivative contains only the partial derivatives of temperature with respect to time and the axial coordinate. To simplify analysis a common sink temperature, \bar{T}_A , and a common overall heat transfer coefficient, U , may be assumed and, as before, the temperature effect on physical parameters is ignored. On the other hand, the electric current and the electrolyte conductivity are considered a priori as functions of the axial coordinate. If the thermal effects of the electrode processes are negligible with respect to other constituents of the heat balance, Equation 4 may be simplified to

$$\frac{\partial T}{\partial t} = -V_x \frac{\partial T}{\partial x} - \frac{U}{S \rho c_p} (T - \bar{T}_A) + \frac{i_x^2}{\rho c_p \sigma_x} \quad (13)$$

provided that the geometric aspect ratio w/S is sufficiently large and there is no heat transfer through the bottom of the electrolyser. If the thermal effects of electrode processes are not negligible, the term $i_x \Delta H_R / S \rho c_p z F$ has to be included on the right hand side of Equation 13. This heat balance cannot be solved rigorously. In a first approximation, if the current density and electrolyte conductivity is replaced by a representative average value i_m and σ_m defined, respectively, as

$$i_m = \frac{1}{L} \int_0^L i_x dx$$

and

$$\sigma_m = \frac{1}{L} \int_0^L \sigma_x dx$$

the resulting linear balance equation

$$\frac{\partial T}{\partial t} = -V_x \frac{\partial T}{\partial x} - \alpha_1 (T - \bar{T}_A) + \alpha_2 \quad (14)$$

may be solved analytically [4] to obtain

$$T = \bar{T}_A + \frac{\alpha_2}{\alpha_1} [1 - \exp(-\alpha_1 t)] \quad \left(\text{where } t < \frac{x}{V_x} \right) \quad (15a)$$

$$T = \bar{T}_A + \frac{\alpha_2}{\alpha_1} [1 - \exp(-\alpha_1 t)] - \frac{\alpha_2}{\alpha_1} \exp\left(-\frac{\alpha_1}{V_x} x\right) \left[1 - \exp\left(-\alpha_1 t - \alpha_1 \frac{x}{V_x}\right) \right] \quad (15b)$$

(where $t \geq \frac{x}{V_x}$)

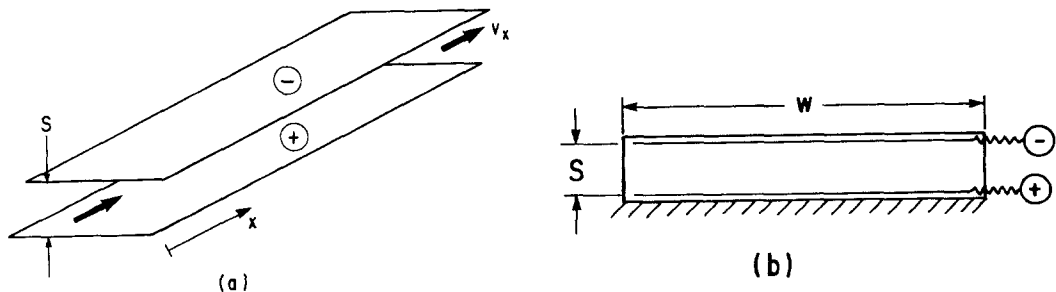


Fig. 1. Sketch of a plug-flow electrochemical reactor. (a) Electrode and flow configuration. (b) View from the entrance side. \ominus cathode; \oplus anode (arbitrary positions).

The steady-state temperature profile along the reactor axis is

$$T_{s,x} = \bar{T}_A + \frac{\alpha_2}{\alpha_1} \left[1 - \exp \left(-\frac{\alpha_1}{V_x} x \right) \right] \quad (16)$$

and the temperature of the exit electrolyte is

$$T_{s,L} = \bar{T}_A + \frac{\alpha_2}{\alpha_1} [1 - \exp(-\alpha_1 \tau)] \quad (17)$$

if τ is the PFER time constant and if the entering electrolyte temperature is \bar{T}_A .

In electrolytic reactors of large conversion (i.e. large current density and long electrodes), average quantities are not sufficient and spatial integration of i_x and σ_x has to be carried out. The steady-state degenerate of Equation 13, with the thermal effect of the electrode reactions:

$$\frac{dT_s}{dx} = -\beta_1(T_s - \bar{T}_A) + \beta_2 \frac{i_x^2}{\sigma_x} - \beta_3 i_x \quad (18)$$

may formally be integrated as

$$T_s = \bar{T}_A + \beta_2 \exp(-\beta_1 x) \int_0^x \frac{i_x^2}{\sigma_x} \exp(\beta_1 x) dx - \beta_3 \exp(-\beta_1 x) \int_0^x i_x \exp(\beta_1 x) dx \quad (19)$$

with the integrals to be evaluated via an appropriate numerical quadrature [5]. Alternatively, if the axial distance can be subdivided into small segments, Δx_k , within which i_x and σ_x may be considered as constants, then at an arbitrary position $x_N = \sum_{k=0}^N \Delta x_k$ measured from the reactor entrance,

$$T_N(x) \cong \bar{T}_A + \beta_2 \exp(-\beta_1 x_N) \sum_{k=0}^N \left(\frac{i_x^2}{\sigma_x} \right)_k \exp(\beta_1 \bar{x}_k) \Delta x_k - \beta_3 \exp(-\beta_1 x_N) \sum_{k=0}^N (i_x)_k \exp(\beta_1 \bar{x}_k) \Delta x_k \quad (20)$$

yields an estimate of the reactor temperature profile. The variation of i_x with an axial coordinate may be obtained as a first approximation from the accompanying material balance [6]; in a more rigorous approach material and heat balance have to be solved simultaneously.

5. Minimization of heat losses

The following sources are prime contributors to the overall enthalpy loss in an electrochemical reactor: combined convection and radiation from the reactor walls, conduction through the reactor bottom to the floor, gassing at the electrodes and evaporation from the (open) electrolyte surface. If the effect of gassing is neglected, the overall rate of enthalpy loss may be written as

$$Q_L = \sum_{j=1}^N U_j A_j (T - T_j) + h_s A_s (T - T_A) \quad (21)$$

If an average heat sink temperature \bar{T}_A can replace T_j , $j = 1 \dots N$ and T_A , a simpler form of Equation 21 is obtained:

$$Q_L = K_0 (T - \bar{T}_A) \quad (22)$$

where K_0 is the overall thermal conductance defined as

$$K_0 \equiv \sum_{j=1}^N U_j A_j + h_s A_s \quad (23)$$

The relatively straightforward estimation of pertinent heat transport coefficients is amply described in the associated literature (e.g. [7]); some caution is to be exercised in estimating h_s since its

numerical value depends on the relative humidity of the surroundings. Unless direct experimental data are available, the relationship [3]

$$h_s = 2.1889 \times 10^{-2} \frac{\Delta H_w}{\Delta T} (P_w - P_\infty)^{1.22} \quad (24)$$

(where P is expressed in kPa; h_s in $\text{W m}^{-2} \text{K}^{-1}$; ΔH_w in kJ kg^{-1} ; ΔT in K or $^\circ\text{C}$) may be used to estimate approximately the specific rate of enthalpy loss via evaporation in an aqueous electrolyte. According to earlier data of Boelter et al. [7] and Pickett [6] the numerical value of h_s varies typically between 30 and $177 \text{ W m}^{-2} \text{K}^{-1}$ for a still surface of water.

In order to minimize enthalpy losses the overall thermal conductance must not exceed a certain value; from an exergy-oriented viewpoint the composite thermal energy cost

$$C_T = C_H Q_L + C_i V_i \quad (25)$$

representing the cost of enthalpy dissipated without recovery and the cost of thermal insulation on the reactor attains its minimum value when its derivative with respect to the insulation thickness, d_i , becomes zero. The enthalpy content of the electrolyte, saved in this manner, can be utilized in another sector of the electrochemical plant, e.g. by preheating some other process fluid. In a rectangular electrolyser of effective side dimensions $S_1 \times S_2$ insulated only on its sides the optimal value of the insulation thickness is obtained for a specified temperature drop ΔT [8, 9] as the physically meaningful root of the cubic equation

$$4d_i^3 + (S_1 + S_2)d_i^2 - k_i \Delta T (S_1 + S_2) \frac{C_H}{C_i} = 0 \quad (26)$$

Table 1 illustrates thermal optimality conditions for a CSTER with $S_1 = 1 \text{ m}$ and $S_2 = 0.5 \text{ m}$; the thermal conductivity of the insulator is taken as $0.04 \text{ W m}^{-1} \text{K}^{-1}$. If the Joule heat generation component is preset by the optimization formula of Ibl [10]

$$I_{\text{opt}}^2 R = \frac{a_s}{b_s} A_E \quad (27)$$

as a starting point, then the right-hand side of Equation 7 must match its left-hand side replaced by Equation 27 under steady-state conditions which minimize C_T in Equation 25, with ΔT and $d_{i,\text{opt}}$ linked via Equation 26 (a detailed numerical illustration is given in [9]).

In the instance of a PFER the same analysis becomes more complicated due to the axially varying steady-state temperature. In this instance Equation 18 has to be solved simultaneously with the mass balance or substance balance equation, employing various values of β_1 , β_2 and β_3 associated with a specific insulation thickness. A reasonable first estimate of the optimal insulation thickness might

Table 1. The variation of optimal insulation thickness (via Equation 26) on a rectangular-shaped electrolyser with unit cost ratios and temperature drop

ΔT ($^\circ\text{C}$)	$d_{i,\text{opt}}$ (cm) at different C_H/C_i ratios		
	0.003	0.005	0.007
10	3.32	4.24	4.97
15	4.03	5.14	6.02
20	4.62	5.88	6.88
25	5.14	6.53	7.63

$$S_1 = 1.0 \text{ m}; S_2 = 0.5 \text{ m}; k_i = 0.04 \text{ W m}^{-1} \text{K}^{-1}; L = 1 \text{ m}.$$

Table 2. The effect of electrolyser geometry on the optimal insulation thickness

T ($^{\circ}\text{C}$)	$d_{i,\text{opt}}$ (cm) at $C_H/C_i = 0.005$	
	Rectangular reactor	Cylindrical reactor
10	4.24	4.25
15	5.14	5.16
20	5.88	5.91
25	6.53	6.56

Rectangular reactor: $S_1 = 1.0\text{ m}$; $S_2 = 0.5\text{ m}$; $L = 1\text{ m}$;
 $k_i = 0.04\text{ W m}^{-1}\text{ K}^{-1}$
 Cylindrical reactor: $r = 0.4\text{ m}$; $L = 1\text{ m}$; $k_i = 0.04\text{ W m}^{-1}\text{ K}^{-1}$.

be obtained if an average current density and electrolyte conductivity are taken and an average steady-state temperature is computed via Equation 28:

$$\bar{T}_S \equiv \frac{1}{L} \int_0^L T_{S,x} dx = \frac{\alpha_2}{\alpha_1} + \frac{\alpha_1 \tau + 1}{\alpha_1 \tau} \bar{T}_A - \frac{1}{\alpha_1 \tau} T_{S,L} \quad (28)$$

Then by putting $\Delta T \cong \bar{T}_S - \bar{T}_A$, a first approximation to $d_{i,\text{opt}}$ can be obtained from Equation 26 as a guide for the recursive solution scheme in which the axial profiles would be considered.

The geometric shape of the electrolyser exerts a minor effect on the optimal insulation thickness, as indicated in Table 2 for the case of a rectangular and cylindrical reactor of the same effective volume. The relative magnitude of the electrolyte flow enthalpy change is, on the other hand, a much more important factor: the lower the electrolyte flow rate the larger the proportion of thermal energy dissipated into the surroundings due to the increase in the overall temperature driving force and, in consequence, the computed value of the optimal insulation thickness is also larger at a fixed C_H/C_i ratio.

6. Batch electrolysers

In the absence of electrolyte flow the heat balance has a simpler mathematical form, as indicated by Equations 9 and 10, but the steady-state equations must be handled with some caution. If electrolysis is carried out over a sufficiently long time so as to reduce significantly the starting electrolyte concentration, the electrolyte resistance and the Joule heat contribution ($I^2 R_e$) will be time-dependent quantities; in fact, thermal steady state will never be reached. In a rigorous analysis the material and heat balances must be solved simultaneously if a certain conversion is specified for the electrode reaction of interest. In a first approximation to the problem, however, and if the electrolytic conversion is small, an average constant value of the $I^2 R_e$ term may be assumed and the steady-state temperature estimated by a relatively simple iteration procedure. Assuming an average mass evaporation rate \bar{m} from an aqueous electrolyte, Equation 9b may be written as

$$I^2 R_e = \bar{m} \Delta H_w + UA(T - \bar{T}_A) + \frac{I \Delta H_R}{zF} \quad (29)$$

where A is the total heat transfer area of the convecting–radiating surfaces and U is the overall convective–radiative heat transfer coefficient pertaining to such surfaces (the evaporation losses are assumed to be negligible with respect to the electrolyte mass). Since ΔH_w may be correlated to temperature by a linear regression

$$\Delta\hat{H}_w = a + bT \quad (30)$$

over reasonably large temperature intervals (e.g. in the 40–60°C range, $a = 2501.5 \text{ kJ kg}^{-1} \text{ H}_2\text{O}$ and $b = -2.386 \text{ kJ kg}^{-1} \text{ K}^{-1}$ with a correlation coefficient of -0.9994 based on steam tables [11]) the first estimate of the steady-state electrolyte temperature is

$$T_s = \frac{I^2 R_c - \bar{m}a + UA\bar{T}_A - \frac{I\Delta H_R}{zF}}{UA + \bar{m}b} \quad (31)$$

Similar simplifications are feasible if the variation of electrolyte resistance with temperature can be represented by a simple regression equation

$$\sigma = \alpha_4 + \beta_4 T \quad (32)$$

within a certain temperature interval. Then, the steady-state electrolyte temperature is the positive root of the second-order algebraic equation

$$T^2 + \frac{\bar{m}(a\beta_4 + \alpha_4 b) + \alpha_4 UA + \beta_4 UA\bar{T}_A + \frac{\beta_4 I\Delta H_R}{zF}}{\bar{m}\beta_4 b + \beta_4 UA} T + \frac{\bar{m}\alpha_4 a + \alpha_4 UA\bar{T}_A + \frac{\alpha_4 I\Delta H_R}{zF} - I^2 C}{\bar{m}\beta_4 b + \beta_4 UA} = 0 \quad (33)$$

where C is the resistance shape factor (i.e. $R_c = C/\sigma$). Equations 29–33 offer useful first approximations to the thermal analysis of a batch system with large enthalpy transfer, e.g. molten-salt electrolytic processes.

7. Concluding remarks

The foregoing treatment of the thermal behaviour provides a basic framework for a thermally proper design of electrochemical reactors. A rigorous approach, accounting for spatial variations of electrolyte temperature and the effect of temperature on various physical properties of the electrolytes requires a comprehensive numerical solution (via finite-difference or finite-element methods) using a digital computer. The CSTER and PFER models are useful, however, as order-of-magnitude first approximations: in many practical situations the model equations will yield temperature profiles of acceptable engineering accuracy from the point of view of heat economy.

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