

Stability and transient response of an electrolytic reactor

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Using a continuous flow stirred tank electrochemical reactor model, the stability and transient response of electrolytic reactors is analysed in terms of a Liapunov function and digital simulation.

Nomenclature

A_E	electrode area	T	electrolyte temperature; T_i its inlet values, T^* its steady state value
A_i	reactor wall area; $i = 2, 3, 4, 5$ denote the four vertical walls of a rectangular tank; A_1 is tank bottom area; A_6 is area of the electrolyte surface	T_A	ambient temperature
b	slope of the polarization curve	T_F	floor temperature
c	electrolyte concentration; c_i its inlet value; c^* its steady state value	t	time
C_p	specific heat of the electrolyte	U	voltage drop
d_1	thickness of the reactor walls	U_i	wall-to-ambient overall heat transfer coefficient associated with wall A_i
F	Faraday's constant	$V(\mathbf{x})$	Liapunov function
G	electrolyte mass flow rate	V_t	active reactor volume (free electrolyte volume)
h_6	heat transfer coefficient associated with electrolyte surface A_6	x_1	dimensionless temperature
I	electric current	x_2	dimensionless concentration
k	geometric aspect ratio (electrode separation distance divided by electrode area)	z	valency
k_1	thermal conductivity of the reactor wall	α, β	lumped parameters defined by Equations 19a and b
m_e	mass of the electrolyte in the reactor	ΔH_R	heat of reaction
Q	quantity defined by Equation 8a	ϵ, δ	parameters of the Liapunov matrix
Q_L	rate of heat dissipation	γ	quantity defined by Equation 8e
q	electrolyte volumetric flow rate	Γ	quantity defined by Equation 9a
R	quantity defined by Equation 8b	θ	dimensionless time
R_e	electrolyte resistance	ρ	electrolyte density
S	quantity defined by Equation 8c	σ	electrolyte conductivity
		ϕ^*	quantity defined by Equation 9b
		ψ	quantity defined by Equation 8d
		<i>Special symbols</i>	\dot{x}_1, \dot{x}_2 derivatives of x_1 and x_2 with respect to θ (Equation 12)

1. Introduction

The analysis of the transient behaviour of electrochemical reactors has hitherto received relatively scant attention in terms of unsteady-state mathematical models, although such models have potential applications in the study and optimization of start-up and shut-down procedures, and temporary deviations from set operating conditions in an electrochemical plant. They also serve as basis for the under-

standing of the dynamics of electrochemical processes [1–4]. The rigorous treatment of electrochemical process transients is characteristically cumbersome due to the nonlinear nature of the governing differential equations and interlocking nonlinear algebraic relationships. This mathematical complexity has been well illustrated in the instance of transient natural convection [5, 6]; simplified transient models, on the other hand, have been used with reasonable success in a number of electrolytic systems, e.g. packed bed electrodes [7]. Certain aspects of deviation from steady state continuous flow stirred tank electrochemical reactors (CSTER) and plug-flow reactors have been briefly discussed by Pickett [8] from a reactor-operation point of view.

One of the pertinent questions regarding transient behaviour is the stability of the steady state, i.e. whether a system perturbed out of its set operating conditions will or will not return to its steady state. In electrochemical reactors perturbations occurring in current or voltage, concentration, flow rate or composition of the electrolyte will generate a transient operation which can be described in terms of appropriate mathematical models. Reactor stability is a well established concept in chemical engineering (see e.g. [9]) but it has not been treated in depth so far in the electrochemical reactor literature. The purpose of this paper is to demonstrate the power of transient modelling techniques and stability theory in dealing with electrochemical reactors; they can serve as a useful tool in the rational design of start-up and shut-down of such reactors, and the regulative control of their operation. A specific reactor type of CSTER was chosen as a working example in order to keep the mathematical involvement at a manageable size. This reactor model has been widely discussed in the literature and its unsteady-state thermal behaviour has been the subject matter of recent publications [10, 11].

2. Transient and steady state behaviour of CSTER

The reactor vessel considered is a rectangular tank containing a single pair of parallel plate electrodes. It is assumed that sufficient mixing via mechanical means or otherwise exists in the system to allow the lumped-parameter based CSTER approximation to describe the variation of electrolyte temperature and concentration with time. Electrolysis occurs either in a galvanostatic or a potentiostatic mode and there is one dominant reaction occurring at each electrode. Then, the CSTER model consists of a mass balance and a thermal balance; in the unsteady state these equations may be written, respectively, as

$$V_t \frac{dc}{dt} = qc_i - qc - \frac{I}{zF} \quad (1)$$

$$m_e C_p \frac{dT}{dt} = GC_p T_i - GC_p T - Q_L + I^2 R_e - \frac{I \Delta H_R}{zF} \quad (2)$$

where the heat dissipation term may be expanded to

$$Q_L = \frac{k_1}{d_1} A_1 (T - T_F) + \sum_{i=2}^5 U_i A_i (T - T_A) + h_6 A_6 (T - T_A) \quad (3)$$

in a rectangular tank. Moreover, the electrolyte resistance may be expressed as

$$R_e = \frac{k}{\sigma} \quad (4)$$

where σ is, of course, a function of c and T . We assume that the $\sigma(c, T)$ relationship is available as an appropriate regression constructed on the basis of experimental data.

It will be advantageous to think in terms of dimensionless perturbation variables

$$x_1 \equiv (T - T^*)/T_i \quad (5a)$$

$$x_2 \equiv (c - c^*)/c_i \quad (5b)$$

and dimensionless time $\theta = tq/V_t$, where (c^*, T^*) is a steady state of reactor operation. Then, the balance equations may be rewritten as

$$\frac{dx_1}{d\theta} = -\psi x_1 + R - S \quad (6)$$

$$\frac{dx_2}{d\theta} = -x_2 - Q \quad (7)$$

where

$$Q \equiv \frac{1}{zF_t c_i q} (I - I^*) \quad (8a)$$

$$R \equiv \frac{kV_t}{m_e C_p T_i q} \left(\frac{I^2}{\sigma} - \frac{I^{*2}}{\sigma^*} \right) \quad (8b)$$

$$S \equiv \frac{\Delta H_R V_t}{m_e C_p z F T_i q} (I - I^*) \quad (8c)$$

$$\psi' \equiv \frac{G}{m_e} + \frac{k_1 A_1}{m_e C_p d_1} + \frac{\sum_{i=2}^5 U_i A_i}{m_e C_p} + \frac{h_6 A_6}{m_e C_p} \quad \psi = \frac{V_t}{q} \psi' \quad (8d)$$

$$\gamma \equiv \frac{q}{V_t} = \frac{G}{m_e} \quad (8e)$$

If we define, in addition, the parameters

$$\Gamma^* \equiv \frac{G}{m_e} + \frac{\sum_{i=1}^5 U_i A_i + h_6 A_6}{m_e C_p} \cdot \frac{T_A}{T_i} + \frac{k_1 A_1}{m_e C_p d_1} \cdot \frac{T_F}{T_i} \quad (9a)$$

$$\phi^* \equiv \frac{kI^{*2}}{m_e C_p \sigma^* T_i} - \frac{\Delta H_R I^*}{m_e C_p z F T_i} \quad (9b)$$

then the steady-state conditions, i.e. where

$$\frac{dx_1}{dt} = \frac{dx_2}{dt} = 0 \quad \text{or} \quad \frac{dx_1}{d\theta} = \frac{dx_2}{d\theta} = 0, \quad \text{can be expressed as}$$

$$c^* = c_i - \frac{I^*}{\gamma z F V_t} \quad (10a)$$

and

$$T^* = T_i \frac{\Gamma^* + \phi^*}{\psi'} \quad (10b)$$

In this development the tacit assumption (to be verified in a specific reactor) was made that m_e and C_p are essentially independent of c and T within the region of perturbations. Equations 6–8 are descriptors of the time variance of the temperature and concentration deviations from the steady state prevailing before a perturbation in the system has occurred.

3. Stability analysis of CSTER behaviour

The prime concern of stability analysis is to predict the end result of a disturbance occurring in a physical system: will the system eventually reach the same steady state, or a different steady state; will it oscillate or at worst, will it suffer physical destruction? Secondly, how is the transient behaviour affected by the amplitude of the perturbation? These questions can be answered usually without much difficulty if the system can be described adequately via a linear mathematical model by solving the linear differential equations and computing $(\lim x_1; t \rightarrow \infty)$ and $(\lim x_2; t \rightarrow \infty)$. In nonlinear systems this

approach can be *very* cumbersome and time consuming because no general conclusions can be drawn from a solution associated with a particular form of perturbation. Modern stability theory [12, 13] employs methods divorced from the actual solution of differential equations; one powerful method is based on Liapunov's theory of stability [9, 12–16], in terms of *algebraic* Liapunov functions. As shown in Appendix A, Liapunov-based analysis of stability requires a relatively modest amount of algebraic computation. The method has found widespread applications in mechanics, space exploration, process control and chemical reactor engineering; it is beyond the scope of this paper to discuss the wealth of literature on this subject matter.

Among various families of Liapunov functions explored in the literature, quadratic forms related to the total energy concept are usually the simplest to manipulate. Following the discussion in Appendix B, a positive definite symmetric matrix Q with *a priori* indeterminate elements ϵ and δ , $Q = \begin{pmatrix} 1 & \epsilon \\ \epsilon & \delta^2 \end{pmatrix}$ is chosen such that $\delta^2 - \epsilon^2 > 0$. Then,

$$V(x_1, x_2) = (x_1 \ x_2) \begin{pmatrix} 1 & \epsilon \\ \epsilon & \delta^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad (11)$$

with its time derivative

$$\frac{dV}{d\theta} = (\dot{x}_1 \ \dot{x}_2) \begin{pmatrix} 1 & \epsilon \\ \epsilon & \delta^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + (x_1 \ x_2) \begin{pmatrix} 1 & \epsilon \\ \epsilon & \delta^2 \end{pmatrix} \begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \end{pmatrix} \quad (12)$$

Using Equations 6 and 7, Equation 12 may be written directly as

$$\frac{1}{2} \cdot \frac{dV}{d\theta} = x_1[-\psi x_1 + R - S + \epsilon(-x_2 - Q)] + x_2[\epsilon(-\psi x_1 + R - S) + \delta^2(-x_2 - Q)] \quad (13)$$

for the system discussed in this paper. Consider now a specific class of perturbations: a sudden change in the electrolyte temperature and/or concentration occurs in the CSTER. This perturbation is represented mathematically by 'initial' conditions x_1^0 and x_2^0 ; the problem is now to find the region in the (x_1, x_2) plane wherein any x_1^0, x_2^0 perturbation will let the CSTER eventually regain its previous steady state $(0, 0)$ corresponding to (c^*, T^*) . Inspection of Equation 11 indicates that the $V(x_1, x_2) = 0$ and $\lim V(x_1, x_2) = \infty$ as $x_1 \rightarrow \infty, x_2 \rightarrow \infty$ conditions are immediately satisfied, hence asymptotic stability is guaranteed wherever the $dV/d\theta < 0$ condition is met. The question of stability is thus reduced to a careful analysis of Equation 13. In many practical electrolytic processes the current-voltage relationship is linear: $I = bU$, where b is a parameter whose numerical value depends on the electrode separation distance, electrolytic concentration and temperature. In a first approximation we may assume that b remains reasonably independent of x_1 and x_2 ; then, Equation 8 can be handled similarly to the galvanostatic case, except that U replaces I , U^* replaces I^* (isomorphic representation) and the coefficient b is incorporated in appropriate terms. The principle of the approach is, therefore, invariant with respect to the mode of electrolysis.

4. Illustrative example: electrodeposition of copper by galvanostatic electrolysis

Table I summarizes the operating conditions of a CSTER where copper is deposited on a metal cathode and oxygen is generated at an indifferent anode. The density of the electrolyte is related [17] to composition and temperature by the equation

$$\rho = 1014.3 + 0.1484c - 0.5T \text{ kg m}^{-3} \quad (14)$$

and its electrical conductance by the regression relationship

$$\sigma = 6.5676 \times 10^{-3} c^{0.706} T^{0.55} \text{ S m}^{-1} \quad (15)$$

Equation 15 is based on 88 tabular data entries [17]; the coefficient of correlation is $r = 0.988$ within the $98.9 < c < 1322$ and $20 < T < 70$ range. In both Equations 14 and 15 the unit of concentration is

Table 1. Parameters of cathodic copper deposition in a CSTER under galvanostatic conditions

Reactor	Thickness of polyethylene tank walls: $d_1 = 0.007$ m Vessel size: 0.7 m \times 0.7 m \times 0.7 m Free (electrolyte) volume: $V_t = 0.3881$ m ³ Thermal conductivity of tank walls: $k_1 = 0.313$ W m ⁻¹ K Wall-to-ambient heat transfer coefficient: $h = 4.61$ W m ⁻² K Electrolyte surface evaporation heat transfer coefficient: $h_g = 18$ W m ⁻² K Reactor geometry factor: $k = 1.47$ m ⁻¹
Electrodes	Separation distance: $s = 0.68$ m Active electrode area: 0.68 m \times 0.68 m (0.4624 m ²) Thickness: 0.002 m
Electrolyte	Aqueous copper sulphate Average density: $\bar{\rho} = 1096.5$ kg m ⁻³ Mass in reactor: $m_e = 425.5$ kg Average specific heat: $C_p = 4186$ J kg ⁻¹ K ⁻¹ Heat of overall reaction: $\Delta H_R = 221.6$ kJ mol ⁻¹ Cu
Operating Conditions	Inlet electrolyte concentration: $c_i = 850$ mol m ⁻³ Electrolyte flow rate: $G = 3 \times 10^{-4}$ kg s ⁻¹ Electric current: $I = 41.6$ A (18% of limiting current) Inlet electrolyte temperature: $T_i = 25^\circ$ C Ambient temperature: $T_A = 20^\circ$ C Floor temperature: $T_F = 20^\circ$ C

mol m⁻³ and the unit of temperature is celsius. In consequence, $\psi' = 0.08289$ h⁻¹; $\gamma = 2.538 \times 10^{-3}$ h⁻¹; $T_i \Gamma^* = 1.67076$ K h⁻¹; $T_i \phi^* = 5.14169/\sigma^* - 0.09655$ K h⁻¹. Then, Equation 10a yields $c^* = 62.06$ mol m⁻³ and Equation 10b becomes $T^* = 18.9115 + [512.24/(T^*)^{0.55}]$ which yields, via an appropriate root-search procedure, the value of $T^* = 69^\circ$ C.

We shall proceed now to the test of stability by establishing the range (x_1, x_2) where a perturbation in c or T (or both) corresponding to initial perturbation state (x_1^0, x_2^0) will cause the reactor to return to its steady state $c^* = 62.06$ mol m⁻³; $T^* = 69^\circ$ C i.e. $x_1 = 0, x_2 = 0$. Rewriting Equation 13 as

$$\frac{1}{2} \frac{dV}{d\theta} = -\psi x_1^2 - \delta^2 x_2^2 - \epsilon(\psi + 1)x_1 x_2 + R(x_1 + \epsilon x_2) \quad (16)$$

it becomes obvious that one logical condition for its negative definiteness value is $-\epsilon(\psi + 1)x_1 x_2 + R(x_1 + \epsilon x_2) < 0$, since the first two terms are always negative. However, the resulting condition

$$\frac{1}{\epsilon} x_1 + x_2 \leq \frac{\psi + 1}{R} x_1 x_2 \quad (17)$$

leads to unacceptable results: if, e.g. ϵ is too large, negative values of x_1 would be excluded and if ϵ is too small, negative values of x_2 would be excluded. It is better, therefore, to search for conditions which will render $dV/d\theta$ negative via *summation* of the four terms. As a first choice, $\epsilon = 0$ may be set in order to simplify this search. Then Equation 14 degenerates to

$$\frac{1}{2} \frac{dV}{d\theta} = -\psi x_1^2 - \delta^2 x_2^2 + R x_1$$

with its numerical equivalent of

$$\frac{1}{2} \frac{dV}{d\theta} = -32.687 x_1^2 - \delta^2 x_2^2 + \left(\frac{81.02919}{\sigma} - 65.18425 \right) x_1 \quad (18)$$

where σ is computed via Equation 15. A thorough numerical analysis of the $R x_1$ term indicates that it

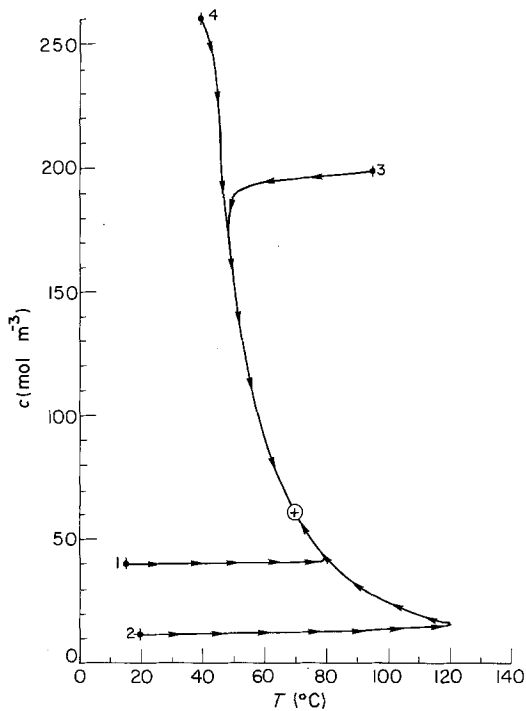


Fig. 1. Transients originating from four different initial states in the reactor of the numerical illustration. The symbol + denotes the globally stable steady state.

is zero at the steady state, along the positive x_2 axis, negative along the negative x_1 axis and mostly positive within the rectangular domain defined by the (x_1, x_2) set for which the regression Equation 15 is valid. Its maximum value within this domain is 98.625 at the corner point $x_1 = -1.96$, $x_2 = 1.482$ (corresponding to $T = 70$ and $c = 98.9$). For each interior point as well as along the boundaries of this rectangular domain the ψx_1^2 product is sufficiently large to force negative definiteness on V if the numerical value of δ is chosen to be sufficiently large. To obtain the 'safest' value of δ , we search for the largest positive value of the $(-\psi x_1^2 + R x_1)$ term which is found to be 24.04 at $x_1 = -0.85$, $x_2 = 1.482$ (boundary point). The numerical value of this term decreases gradually to negative values as x_2 is decreased at $x_1 = -0.85$, the cross over point being around $x_2 = 0.138$. Hence, $\delta > 3.4$ will render Equation 18 negative everywhere in the (x_1, x_2) domain of interest; the exact numerical value of δ is immaterial. It follows immediately that the electrolytic process in the illustrative example is asymptotically stable in the domain of electrolyte temperature and concentration for which the regression relationship of the electrolyte conductivity, Equation 15, is valid. It is important to note that the process may be asymptotically stable in a wider range of x_1 and x_2 , but the constraints on Equation 15 do not permit a *rigorous* numerical analysis for an extended domain. The Liapunov function-based approach is, of course, not responsible for this limitation.

It is instructive to compare the results of Liapunov analysis to predictions via simulation. The transient behaviour of this reactor is illustrated in Fig. 1, showing return to the steady state from four different initial perturbation states. The trajectories were obtained from a digital computer simulation of the dynamic equation set

$$\frac{dx_1}{dt} = -0.08289x_1 + \frac{0.20567}{\sigma} - 0.16545 \text{ h}^{-1} \quad (19a)$$

$$\frac{dx_2}{dt} = -0.002538x_2 \text{ h}^{-1} \quad (19b)$$

where σ is assumed to obey Equation 15 in the (x_1, x_2) range of interest and the numerical values in

Table 1 were employed in establishing the numerical values shown. Equation 19b can, of course, be integrated analytically to

$$x_2 = x_2^0 \exp(-0.002538t) \quad (20)$$

and x_2 may directly be substituted into Equation 15; the savings in time, however, are minimal for a fast computer. The sudden decrease in temperature (initial states 1 and 2) results in a sharply reduced electrolyte conductivity, hence a sharp increase in the rate of Joule heat generation since the current is kept constant. As the electrolyte temperature increases, so does the rate of heat transmission to the surroundings and the temperature begins to drop eventually towards the steady state. The electrolyte concentration increases less rapidly than temperature since the electrolyte flow rate is rather small (although the inlet electrolyte concentration is high). If the sudden decrease in temperature is small (initial state 4) the resulting increase during the transient is less rapid and the overshoot exhibited by trajectory 1 is avoided. When the initial change in temperature is an increase, the sudden drop in electrolyte resistivity results in a decrease in the rate of Joule heat generation and the electrolyte temperature will decrease until the rate of heat transmission to the surroundings has fallen to the point where a slow gradual increase towards the steady state can begin. The final approach to the steady state is independent of the position of the initial state, as shown by the common trajectory portion. The four distinct trajectory portions are somewhat approximate inasmuch as the loss in electrolyte mass due to surface evaporation has not been taken into account for the sake of reducing the complexity of the problem. This error is relatively small in view of the large electrolyte mass.

5. Stability and transient behaviour in potentiostatic electrolysis

When the potential drop between electrodes is kept constant, the mathematical analysis becomes encumbered by the dependence of the polarization slope b on c and T . In this instance an extensive set of polarization curves obtained at various temperatures and concentrations, but using the same electrodes, is required. As before, the S - and Q -derivatives are zero. If the effect of c and T on b is minimal, the analysis degenerates to the galvanostatic case. If the (I, U) relationship is nonlinear the R -derivatives and the entire analysis are more complicated.

6. Small perturbations about the steady state: linear approximation to transient behaviour

When the initial electrolyte temperature and concentration are not too different from their respective steady values, the transient behaviour may be obtained in an analytical form via linearization of Equation 6. In the case of constant-current electrolysis, a linear approximation to R in Equation 8b may be obtained by a truncated Taylor expansion of the electrolyte conductivity term:

$$\frac{1}{\sigma} - \frac{1}{\sigma^*} \simeq -A^*(T - T^*) - B^*(c - c^*) \quad (21)$$

where

$$A^* \equiv \left(\frac{1}{\sigma^2} \frac{\delta \sigma}{\delta T} \right)_{T^*, c^*} \quad \text{and} \quad B^* \equiv \left(\frac{1}{\sigma^2} \frac{\delta \sigma}{\delta c} \right)_{T^*, c^*}$$

are quantities evaluated at steady state conditions. Defining the lumped parameters

$$\alpha \equiv \psi' + \frac{kI^2 A^*}{m_e C_p} \quad (22a)$$

$$\beta \equiv \frac{kI^2 B^* C_0}{m_e C_p T_i} \quad (22b)$$

a linear approximation to Equations 6 and 7 may be written as

$$\frac{dx_1}{dt} = -\alpha x_1 - \beta x_2 \quad (23a)$$

Table 2. Comparison of the linear approximation to rigorous simulation in the numerical illustration

Response time (h)	Electrolyte temperature (°C)	
	Simulation	Linear approximation*
0.05	73.93	73.96
0.55	73.55	73.57
1.05	73.20	73.20
1.55	72.87	72.85
2.05	72.55	72.52
3.05	71.97	71.91
5.05	70.99	70.90

* $\alpha = 0.115\ 861\ \text{h}^{-1}$, $\beta = 0.042\ 331\ \text{h}^{-1}$.

$$\frac{dx_2}{dt} = -\gamma x_2 \quad (23b)$$

for galvanostatic electrolysis. The analytical solution in this instance is

$$x_1 = x_1^0 e^{-\alpha t} + \frac{\beta x_2^0}{\alpha - \gamma} [\epsilon^{-\alpha t} - \epsilon^{-\gamma t}] \quad (24a)$$

$$x_2 = x_2^0 e^{-\gamma t} \quad (24b)$$

In Table 2 electrolyte temperatures predicted via rigorous simulation and by Equation 24a are compared for the reactor illustrated numerically, in the specific case of $T^0 = 74^\circ\text{C}$ and $c^0 = 67.06\ \text{mol m}^{-3}$. The two predictions remain very close for essentially the entire trajectory (except for the immediate neighbourhood of the steady state where the linear approximation cannot predict a slight temporary 'undershoot' below the steady state temperature). The linear approach must be applied with caution; in the case of perturbation 3 in Fig. 1, for example, the linear approximation of 85.6°C compares poorly with the rigorously simulated temperatures of 90.3°C at $t = 1.05\ \text{h}$. Here, the perturbed state is too far from the steady state for a linear approximation.

7. The speed of transient response to a perturbation

Inspection of Equation 6 and 7 indicates that the speed of the transient response of the reactor described by the CSTER model is determined by parameters ϕ and γ ; it follows from Equations 8d and 8e that unless heat losses from the reactor are considerably large, the rate at which the perturbed reactor reapproaches its steady state depends essentially on the mass flow rate to electrolyte mass ratio. Phrased otherwise, the reactor time constant is approximately m_e/G if heat losses are modest (the case of a well insulated reactor). Thus, fast return to the steady state can be expected when the reactor free volume is relatively small and the electrolyte flow rate is relatively high. The numerical illustration is a converse case with a relatively large time constant (about 390 h).

8. Concluding remarks

The foregoing analysis can be extended to perturbations in 'forcing' variables, such as electrolyte flow rate, inflow electrolyte concentration, inflow electrolyte temperature and electric current, although the study of stability becomes more involved mathematically. The treatment of these cases is beyond the scope of the current paper. Stability and transient behaviour are important parameters for the understanding of fluctuations in reactor performance and for the rational design of (computer-based) reactor

control. The subject matter is of obvious significance for the eventual automation of certain electrochemical plants.

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Appendix A

A summary of Liapunov's stability theorem

A dynamic system described by the differential equation set

$$\frac{dx}{dt} = f(x) \quad (\text{A1})$$

where x is a vector whose elements are the so-called state variables, is asymptotically stable within a specific region Γ if there exists at least one scalar function $V(x)$ satisfying the following conditions:

$$(a) \quad V(x) > 0 \text{ for } x \neq 0 \quad (\text{A2})$$

$$(b) \quad \frac{dV}{dt}(x) < 0 \text{ for all } x \neq 0 \text{ in } \Gamma \quad (\text{A3})$$

$$(c) \quad \lim_{\|x\| \rightarrow \infty} V(x) = \infty \text{ for every solution in } \Gamma \quad (\text{A4})$$

$(\|x\| \text{ is the norm of vector } x)$

The region Γ is called the region of asymptotic stability. If Γ comprises the entire vector space x , the system is asymptotically stable 'in the large', or globally stable.

Let x^0 be an initial state upon a sudden perturbation of a system resting at steady state $x = 0$ (by translation with respect to some reference conditions, a non zero initial state may be transformed into the null vector); then, if conditions (a)–(c) are satisfied within a region Γ , the system eventually reaches its steady state $x = 0$ regardless of the actual position of x^0 within Γ . The search for stability via Liapunov functions $V(x)$ is much more efficient than attempts to solve Equation A1 for all possible initial conditions x^0 within an appropriate vector space. A rigorous development of the theory summarized briefly here is presented in [16], now a classic in the literature.

One shortcoming of the Liapunov approach is that if a suitable function $V(x)$ cannot be found, it does *not* follow that the system is unstable; however, stability cannot be proved. The strength of the approach is in the reverse case: one single $V(x)$ guarantees stability, at least within a specific region if conditions (a)–(c) are satisfied by this particular $V(x)$.

The size of Γ may well vary with the specific form of a Liapunov function if there are more than one; if one of them indicates global stability, then the system is globally stable and any other forms of $V(x)$, which predict a finite Γ , become immaterial. Construction strategies for Liapunov functions was a fertile research area several years ago; Appendix B summarizes one important construction method particularly useful for nonlinear systems.

Consider, as an illustrative example, the linear second order set of equations [18]

$$\frac{dx_1}{dt} = -2x_1 + x_2 \quad (\text{A5})$$

$$\frac{dx_2}{dt} = x_1 - x_2 \quad (\text{A6})$$

The Liapunov function $V(x) = x_1^2/2 + x_1x_2 + x_2^2$ satisfies conditions (a)–(c) for *all* values of state

variables x_1 and x_2 ; on the other hand, the Liapunov function $V(\mathbf{x}) = x_1^2 + x_2^2$ defines a finite stability region $\Gamma: 2x_1^2 - 2x_1x_2 + x_2^2 > 0$ within which condition (c) is satisfied. It is not difficult to show that this system indeed possesses global asymptotic stability as indicated by the first $V(\mathbf{x})$.

Appendix B

Liapunov functions of quadratic forms

Consider a dynamic system with state variables x_1 and x_2 such that x_1 represents displacement and x_2 , its time derivative, velocity. Then, the sum of its kinetic and potential energy, $\frac{1}{2}(x_1^2 + x_2^2)$ is always positive, its limit as $\|\mathbf{x}\| = (x_1^2 + x_2^2)^{1/2} \rightarrow \infty$ is infinity and its time derivative must be negative if the system is moving towards a stable steady state, since the energy has to decrease towards its minimum value attained at equilibrium. Thus, the energy of a stable system may be taken as one of its Liapunov functions, and

$$V(\mathbf{x}) = \mathbf{x}'I\mathbf{x} \quad (\text{B1})$$

is a bona-fide Liapunov candidate (\mathbf{x}' is the transpose of vector \mathbf{x}). However, Equation B1 is rather restrictive in predicting the size of the region within which a dynamic system remains asymptotically stable and it may become necessary to begin with *a priori* indeterminate elements in the constitutive matrix of the quadratic form:

$$V(\mathbf{x}) = \mathbf{x}'Q\mathbf{x} \quad (\text{B2})$$

where Q has to be positive definite. Let the dynamic system be represented by the vector equation $d\mathbf{x}/dt = f(\mathbf{x})$. Then its Liapunov derivative is obtained by differentiating Equation B2

$$\frac{dV}{dt} = f'Q\mathbf{x} + \mathbf{x}'Qf \quad (\text{B3})$$

Since the elements of the Q matrix are *a priori* indeterminate, a convenient choice is the following: $q_{11} = 1$, $q_{12} = q_{21} = \epsilon$ and $q_{22} = \delta^2$ such that $\delta^2 - \epsilon^2 > 0$. Then, Q is positive definite. In the specific case of a second order system, Equation B3 has the following form, upon differentiation and algebraic manipulation:

$$\frac{dV}{dt} = 2[x_1(f_1 + \epsilon f_2) + x_2(\epsilon f_1 + \delta^2 f_2)] \quad (\text{B4})$$

Equation 13 is the specific form of Equation B4 for the electrolytic reactor considered in this paper.

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