

# *A mathematical model for non-ideal tank electrolysers*

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An approximate mathematical model, based on the equivalent gain principle for stochastic process dynamics, has been developed to analyse the behaviour of tank electrolysers not amenable to CSTER-modelling.

## Nomenclature

	$r(t)$	composite input
	$s^2$	sample variance (Table 2)
$a_k, b_k$	expansion coefficients	$\text{sgn}(z)$ positive sign for $z > 0$ and negative sign for $z < 0$
$c$	electrolyte concentration in tank electrolyser	$t$ time
$c_e$	exit electrolyte concentration	$x(t)$ input function; $x_0$ its magnitude (time-invariant)
$c_i$	inlet electrolyte concentration	$y(t)$ output function
$d(t)$	distortion function (Equation 1)	$z$ valency
$F$	Faraday's constant	$\alpha_1$ $(c_i - c_i^*)/q^*$
$f(x)$	non-linear function of input $x(t)$	$\alpha_2$ $1/zFq^*$
$\hat{f}(m)$	shorthand for function in Equation 20	$\alpha_3$ $1/q^*$
$I$	electric current	$\sigma^2$ variance of input $x(t)$
$K$	equivalent gain (Equation 4)	$\tau$ mean residence time of tank electrolyser ( $\tau = V/q^*$ at steady state)
$k$	linear coefficient; as subscript it denotes a harmonic element. $k_1$ and $k_2$ , lumped parameters (Equation 27)	$\tau_a$ apparent time constant of tank electrolyser
$m$	exponent (rational number)	$\phi(j\omega)$ Fourier transform of impulse response of the tank electrolyser (Equation 16)
$p(x)$	amplitude probability density of function $x(t)$	$\Psi(\omega)$ power spectral density (Equation 16)
$q$	volumetric flow rate of electrolyte	

## 1. Introduction

In recent years much progress has been made in both development and applications of the CSTER (continuous-flow stirred-tank electrochemical reactor) model in electrochemical engineering (e.g. [1-3]), including a relatively new subject: CSTER process dynamics (e.g. [4]). One important limitation of CSTER-based modelling is the existence of non-uniform flow and concentration patterns in tank electrolysers without mechanical mixing, especially in the presence of membranes and separators. Unless the distribution of electrolyte flow has been carefully designed to approach uniformity, and if gas evolution which can also cause sharp local flow and concentration gradients is not excessive, the mathematical description of a tank electrolyser via a CSTER model may be severely inaccurate.

One means of accounting for deviation from CSTER conditions would be the classical residence time distribution or exit age distribution approach, well documented in the chemical reaction engineering literature (e.g. [5, 6]), although it has not yet been shown if these techniques can be extended in a straightforward fashion to electrochemical reactors. At any rate, in the absence of

mechanically induced mixing, the estimation of the exit concentration–time relationship is by no means a trivial exercise. An alternative to the residence time distribution or exit age distribution approach to this problem is based on the concept of the equivalent gain in the theory of stochastic process dynamics [7, 8], whose usefulness in the control of non-linear systems has been known for some time [9–11]. The purpose of this paper is to introduce the subject to electrochemical engineering science and to discuss its potential for the analysis and design of real-life tank electrolyzers.

## 2. Theoretical background

Let  $y(t) = f[x(t)]$  denote a non-linear relationship between two time-variant functions  $x(t)$  and  $y(t)$ ; then, the mean square of the distortion between  $y(t)$  and its linear approximation  $kx(t)$ ,

$$d(t) \equiv y(t) - kx(t) \quad (1)$$

may be written as

$$\overline{d^2(t)} = \int_{-\infty}^{+\infty} [f(x) - kx]^2 p(x) dx \quad (2)$$

where  $p(x)$  is the amplitude probability density (APD) of  $x(t)$ . The equivalent gain is the particular value of  $k$  which minimizes the mean square, i.e.

$$\partial \overline{d^2(t)} / \partial k = 0 \quad \text{at } k = K \quad (3)$$

Applying Equation 2 to Equation 3 the relationship

$$K = \frac{1}{\sigma^2} \int_{-\infty}^{+\infty} xf(x)p(x) dx \quad (4a)$$

$$\sigma^2 \equiv \int_{-\infty}^{+\infty} x^2 p(x) dx \quad (4b)$$

is obtained. In particular, if the input  $x(t)$  has a Gaussian APD, Equation 4a reduces to the simpler form [9]

$$K = \frac{1}{\sigma(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \frac{df}{dx} \exp(-x^2/2\sigma^2) dx \quad (5)$$

where  $\sigma^2$  is the variance of the Gaussian input  $x(t)$ . The approach can be generalized to multiple inputs. If there are, for example, two inputs  $x_1(t)$  and  $x_2(t)$  with APD  $p_1(x_1)$  and  $p_2(x_2)$ , respectively, the APD of the summed input  $r(t) = x_1(t) + x_2(t)$  is given by

$$p(r) = \int_{-\infty}^{+\infty} p_2(r - x_1)p_1(x_1) dx_1 = \int_{-\infty}^{+\infty} p_1(r - x_2)p_2(x_2) dx_2 \quad (6)$$

and the equivalent gain is defined by

$$K = \frac{1}{\sigma_1^2 + \sigma_2^2} \int_{-\infty}^{+\infty} rf(r)p(r) dr \quad (7a)$$

where

$$\sigma_i^2 \equiv \int_{-\infty}^{+\infty} x_i^2 p_i(x_i) dx_i; \quad i = 1, 2 \quad (7b)$$

If both inputs are Gaussian, Equation 7a may be rewritten as

$$K = \frac{1}{[2\pi(\sigma_1^2 + \sigma_2^2)]^{1/2}} \int_{-\infty}^{+\infty} \frac{df}{dr} \exp[-r^2/2(\sigma_1^2 + \sigma_2^2)] dr \quad (8)$$

It follows that the minimum value of the mean square error in the case of an even probability

distribution is given by the simple relationship

$$\overline{d^2(t)}_{\min} = 2 \int_0^{\infty} f^2(x)p(x) dx - K^2 \sigma^2 \quad (9)$$

The prime utility of the equivalent gain concept in non-linear control theory is a linear approximation to a non-linear element  $f(x)$ , used for the design of feedback control schemes; if  $f(x)$  and  $p(x)$  are known, the necessary computations are relatively straightforward. For the purposes of this paper, however, the reverse procedure is of interest, i.e. where an equivalent gain is estimated from input and output information.

### 3. Application of the equivalent gain principle to the analysis of non-ideal tank electrolyzers

The overall mass balance in an isothermal tank electrolyser with through-flow may be written as

$$V \frac{dc}{dt} = qc_i - qc_e - \frac{I}{zF} \quad (10)$$

where the electrolyte concentration in the tank,  $c$ , not necessarily uniform, is a function of time. The familiar CSTER model is derived directly from Equation 10 if perfect mixing is assumed; then,  $c = c_e$  and time becomes the only independent variable. It is worth noting that if the flow rate is a process variable, Equation 10 cannot be solved analytically in general even if the CSTER assumption is valid, except in the case of a sudden jump (step perturbation) in  $q$ . In the case of an electrolyser operating under imperfect mixing conditions, no analytical solution of Equation 10 is attainable.

In applying the equivalent gain approach in the simplest sense to this problem, Equation 10 is replaced by a non-linear function element  $c_e = f(q)$ , assuming that flow rate is the only input and the exit electrolyte concentration is considered as the only output. Although not imperative, the use of perturbation (or deviation) variables  $x \equiv q - q^*$  and  $y \equiv c_e - c_e^*$  related to steady-state conditions is preferable: then  $y = f(x)$  and the notation of the previous section immediately applies. Let the APD of the flow-rate perturbation be approximated by a Gaussian form with variance  $\sigma^2$ . In the simplest case the input-output relationship is a symmetric power function

$$f(x) = \text{sgn}(x) \cdot |x|^m \quad (11)$$

and the equivalent gain is obtained from Equation 5 (Appendix 1) as

$$K = \frac{m}{(2\pi)^{1/2}} 2^{m/2} \sigma^{m-1} \Gamma\left\{\frac{m}{2}\right\} \quad (12)$$

The power parameter,  $m$ , can be estimated via a successive approximation or a root-finding procedure if  $K$  and  $\sigma$  have been determined from experimental power spectrum analysis of input and output data (Section 4). If the input-output relationship may be described by a polynomial of the form

$$f(x) = \sum_{k=0}^n a_{2k+1} x^{2k+1} \quad (13)$$

then in the case of a Gaussian input with variance  $\sigma^2$  (Appendix 2),

$$K = \sum_{k=0}^n a_{2k+1} (1.3.5 \dots 2k+1) \sigma^{2k} \quad (14)$$

is the final equivalent gain (Equation 5). The  $a_i$  coefficients are obtained from a power spectrum analysis of the input using a sufficient set of variances (alternatively, the numerical values of  $a_i$  in Equation 13 might be known from an a priori theoretical analysis of the non-linear element).

#### 4. Power spectrum analysis

In the classical approach (e.g. [12, 13]) of spectrum analysis, if input  $x(t)$  has the power spectral density  $\Psi_x(\omega)$  defined as

$$\overline{x^2(t)} \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} \Psi_x(\omega) d\omega \quad (15)$$

then the power spectral density of the output  $y(t)$  of the electrolyser  $\Psi_y(\omega)$  is related to  $\Psi_x(\omega)$  by the relationship

$$\Psi_y(\omega) = K^2 |\phi(j\omega)|^2 \Psi_x(\omega) \quad (16)$$

The function  $\phi(j\omega)$  is the Fourier transform of the impulse response of the electrolyser (Appendix 3). Equation 16 indicates the manner of estimating the equivalent gain from experimental power spectra, which can be obtained by a large variety of modern methods. Of these, real-time spectrum analysis [14–16], autoregressive spectrum analysis [17], the sums-of-delta-function approach [18], digital analysis [19], pulse-sequence analysis [20, 21] and Markov-signal analysis [22] are mentioned as representative examples. The discussion of spectrum analysis is beyond the scope of this paper; general papers of tutorial nature (e.g. [23, 24]) treat this subject in a comprehensive manner.

#### 5. Equivalent gain via harmonic analysis

The equivalent gain may be determined by the reversal of a transformation method [25] proposed originally in the study of non-linear circuit components, if the  $f(x)$  element is contained (e.g. by appropriate normalization) in the  $|x| \leq 1$  domain. Let  $\theta \equiv \omega_0 t$  where  $\omega_0$  is the frequency of a sinusoidal input,  $x = \sin \theta$ , applied to the non-linear element within a low frequency domain. Harmonic analysis of the output provides an empirical Fourier spectrum

$$f(\sin \theta) = \sum_{n=0}^N (\alpha_n \cos n\theta + \beta_n \sin n\theta) \quad (17)$$

Then, using the equivalence

$$f(x) = \frac{a_0}{2} \sum_n [a_n P_n(x) + b_n Q_n(x)] \quad (18)$$

$$P_n(x) \equiv \cos n\theta; \quad Q_n(x) \equiv \sin n\theta$$

$f(x)$  is established by computation and  $K$  is obtained in the usual manner. Since the APD of the sinusoidal function  $x = \sin \theta$  is  $p(x) = 1/\pi(1 - x^2)^{1/2}$ , Equation 4a may be written as

$$K = \frac{2}{\pi} \int_{-1}^{+1} \frac{df}{dx} (1 - x^2)^{1/2} dx \quad (19)$$

since  $\sigma^2 = 0.5$  in this case.

#### 6. Illustrative example

Assume that a tank electrolyser with steady-state operating conditions given in Table 1 is subjected to a stationary random perturbation sequence in the electrolyte flow rate as shown in Table 2 (the numerical values would be obtained by periodic sampling of flow rate via an appropriate instrument-microprocessor assembly). The mean value is very small, hence  $\bar{x} = 0$  is taken for the sake of simplicity and in view of the large sample size,  $s^2 \simeq \sigma^2$  may be assumed. A goodness-of-fit test [26] is performed to test the hypothesis that the sample represents the Gaussian distribution

Table 1. Steady-state operating conditions for the tank electrolyser of the illustrative example

Inlet flow rate	$q^* = 3.412 \text{ l min}^{-1}$
Inlet electrolyte concentration	$c_i = 0.04 \text{ mol l}^{-1}$
Active tank volume	$V = 2001$
Electric current	$I = 50 \text{ A}$
Valency of active ions	$z = 2$
Outlet electrolyte concentration	$c_e^* = 0.0354 \text{ mol l}^{-1}$

[0; 0.7028]; the computed chi-square statistic,  $\chi^2 \approx 2.6$ , is smaller than the critical value of 3.84 at a 95% level of confidence, hence the hypothesis is not rejected. The data permit, therefore, the estimation of  $K$  via Equation 12:

$$K = 0.7028^{m-1} \hat{f}(m) \tag{20}$$

where  $\hat{f}(m) \equiv m/(2\pi)^{1/2} 2^{m/2} \Gamma\{m/2\}$ ; selected values of  $\hat{f}(m)$  are given in Table 3.

Assume that a (quickly performed) power spectrum analysis of the input-output data yields an inaccurate value of  $K = 1.0073$  (the effect of this inaccuracy is shown in Fig. 1). Equation 20 is solved for  $m = 0.7$  and the approximate outlet concentration-flow rate relationship may be written as

$$f(q - q^*) = \text{sgn}(q - q^*) \cdot |q - q^*|^{0.7} \text{ mol m}^{-3} \tag{21}$$

In a more refined approach, several random perturbation sequences with numerically different variances could be considered. Assume that a carefully performed spectral analysis of input-output data obtained in a certain set of measurements yields the results shown in Table 4. This information permits analysis in terms of Equations 13 and 14 with a low numerical value of  $n$ . Setting  $n = 1$ , the coefficients in the appropriate form of Equation 14, i.e.  $K = a_1 + 3a_3\sigma^2$ , are obtained via regression as  $a_1 = 1.154$  and  $a_3 = 1.273$ . The outlet concentration-flow rate relationship is given as

$$f(q - q^*) = 1.157(q - q^*) + 1.272(q - q^*)^3 \text{ mol m}^{-3} \tag{22}$$

Assume finally that harmonic analysis of the output concentration from the tank electrolyser subjected to low-frequency sinusoidal perturbations in the electrolyte flow rate yields the Fourier spectrum (Equation 17)

$$y(t) \cong 2.1587 \sin \theta - 0.3256 \sin 3\theta + 5.625 \times 10^{-3} \sin 5\theta \text{ mol m}^{-3} \tag{23}$$

Equation 23 implies the equivalent forms

$$f(x) = Ax + Bx^3 + Cx^5 \tag{24a}$$

$$= b_1 Q_1(x) + b_3 Q_3(x) + b_5 Q_5(x) \tag{24b}$$

$$= b_1 x + b_3(3x - 4x^3) + b_5(5x - 20x^3 + 16x^5) \tag{24c}$$

Table 2. Stationary random perturbation sequence in inlet flow rate:  $x \equiv q - q^*$  ( $\text{l min}^{-1}$ )

-1.212	0.688	0.088	1.088	-0.212	0.288	-0.412	-0.812
-0.012	-1.812	-0.312	-0.112	0.388	-0.312	1.288	0.288
-0.912	0.888	-0.012	0.188	-0.512	-0.112	0.488	-0.312
-0.112	-0.312	0.288	0.988	-0.212	0.688	-1.512	-0.012
1.288	0.388	-0.212	-0.812	0.488	-0.412	0.788	0.088

Mean:  $\bar{x} = 5 \times 10^{-4}$ .

Standard deviation:  $s = 0.7028$ .

Chi-square of goodness of fit test:  $\chi^2 \approx 2.6$ .

Table 3. Numerical values of the function  $\hat{f}(m) \equiv m/(2\pi)^{1/2} 2^{m/2} \Gamma(m/2)$  at selected values of the independent variable,  $m$

$m$	$\hat{f}(m)$
0.1	0.80415
0.2	0.81360
0.5	0.86012
0.7	0.90620
1.0	0.99975
1.2	1.08046
1.5	1.23280

via Equation 18 and by use of classical trigonometric relationships between multiple angles. Since  $b_1 = 2.1587$ ,  $b_2 = -0.3256$  and  $b_3 = 0.005625$ , the numerical values of  $A = 1.21$ ,  $B = 1.19$  and  $C = 0.09$  are computed. Hence, harmonic analysis yields the outlet concentration-flow rate relationship

$$f(q - q^*) = 1.21(q - q^*) + 1.9(q - q^*)^3 + 0.09(q - q^*)^5 \quad (25)$$

$$|q - q^*| \leq 1 \text{ mol m}^{-3}$$

The plots of Equations 21, 22 and 25, shown in Fig. 1, indicate little divergence between the polynomial forms, but a relatively large deviation from the single-power form (Equation 21), as expected.

A minor refinement of the analysis can be achieved if the independent variable is defined as a fraction of the steady-state flow rate, in terms of the perturbation variable:  $\hat{x} \equiv (q - q^*)/q^*$ . If this option is taken, the equivalent gain analysis yields the relationships

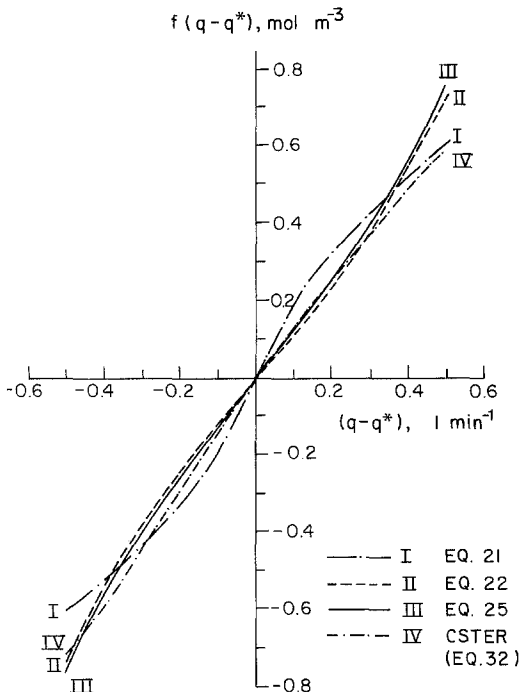


Fig. 1. Exit concentration-inflow rate relationships in the numerical illustration.

Table 4. Equivalent gain values obtained from the spectral analysis of random sequences

Variance ( $\sigma^2$ )	Equivalent gain ( $K$ )
0.685	2.9478
0.692	2.9826
0.713	3.0939
0.721	3.1419

Single power form:

$$f(\hat{x}) = 2.361 \operatorname{sgn} \hat{x} \cdot |\hat{x}|^{0.7} \quad (26)$$

Cubic polynomial form  
(random Gaussian input):

$$f(\hat{x}) = 3.948x + 50.526\hat{x}^3 \quad (27)$$

Cubic polynomial form  
(harmonic analysis):

$$f(\hat{x}) = 4.128\hat{x} + 75.471\hat{x}^3 + 41.619x^5 \quad (28)$$

Similarly, a fractional exit concentration variable,  $y \equiv (c_3 - c_e^*)/c_e^*$ , can be defined and the entire analysis can be carried out in terms of dimensionless variables.

## 7. Comparison with CSTER behaviour

If the CSTER model and small perturbation theory can be applied to a tank electrolyser the overall mass balance (Equation 10) may be rewritten in terms of perturbation variables as

$$\tau \frac{dy}{dt} + y = \alpha_1 x_1 - \alpha_2 x_2 - \alpha_3 x_1 y \quad (29)$$

where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  are lumped parameters,  $\tau = V/q^*$  is the residence time for the tank,  $x_1$  is the perturbation in flow rate and  $x_2$  the perturbation in current. The non-linear term in Equation 29 indicates that analytical solutions are feasible only for step perturbations (i.e.  $x_1 = \text{constant}$ ) in the flow rate. In the simple case of no current perturbation ( $x_2 = 0$ ), the variation of exit concentration with time is given by

$$c_e(t) = c_e^* + k_1[1 - \exp(-k_2 t)] \quad (30)$$

$$k_1 \equiv \frac{\alpha_1 x_0}{1 + \alpha_3(x_0)}; \quad k_2 \equiv \frac{1 + \alpha_3 x_0}{\tau}$$

where  $x_0 \equiv (q_0 - q^*)$ , the magnitude of the flow-rate step, determines both the new steady state and the speed of response of the exit concentration to the step perturbation. Hence, the CSTER response is asymmetric in this case. If there is a simultaneous step perturbation in the current, then  $k_1 = [\alpha_1 x_0 - a_2(I_0 - I^*)]/[1 + \alpha_3 x_0]$  and  $k_2$  is unchanged. Numerical solutions only can be effected if perturbations in the flow rate are of a more complicated nature.

The advantage of the equivalent gain analysis is essentially in the linearization of the  $f(x)$  relationship, allowing a straightforward computation of  $y(t)$ . Since a stirred-tank electrolyser is a first order system (as seen in Equation 10), the approach expresses the variation of the exit concentration with time as a combination of the equivalent gain, which depends on the magnitude of the perturbation in flow rate, and the familiar exponential rise in time. The response of the tank

electrolyser may therefore be written as

$$c_e(t) = c_e^* + K(x_0) \cdot x_0 [1 - \exp(-t/\tau_a)] \quad (31)$$

where  $\tau_a$  is the apparent time constant of the tank, determined from experimental step response or frequency response tests. At very large times, the new steady state

$$\lim_{t \rightarrow \infty} c_e(t) = \begin{cases} c_e^* + k_1 & \text{(CSTER)} \\ c_e^* + K(x_0) \cdot x_0 & \text{(equivalent gain approach)} \\ c_e^* + f(q - q^*) & \text{(rigorous)} \end{cases} \quad \text{Nonideal tank electrolyser} \quad (32)$$

upon perturbation can be estimated without the knowledge of  $\tau_a$ . In consequence, the plots in Fig. 1 may be interpreted as large-time step responses of the tank electrolyser.

## 8. Discussion and critique of the equivalent gain technique

The equivalent gain approach has two major advantages over approaches (e.g. describing function) based on deterministic oscillatory inputs. Firstly, the required analysis can be carried out with on-line perturbations occurring in an electrolytic plant, without having to interrupt normal plant operations. Secondly, it is more general than deterministic linearization techniques and, indeed, it can be easily adapted to sinusoidal input perturbations, for example, as shown in the previous sections. The technique requires a modicum of mathematical manipulations which can be normally carried out on pocket or desk-top devices. On the other hand, adequate instrumentation is necessary for the acquisition of reliable data and for the performing of spectrum analysis.

Certain structurally inherent limitations warrant caution in the case of random inputs. Firstly, their statistical properties should be time-independent; if the perturbation is non-stationary the APD function cannot be reliably constructed. The second problem lies in the fact that the APD cannot furnish information about the probability of temporal transitions from one amplitude to another amplitude [9]. Finally, the nature of the non-linearity,  $f(x)$ , determines the degree of distortion of the APD of the input perturbation; in principle, the output  $y = f(x)$  does not have the same APD as  $x(t)$ . This problem is not important if the system behaves as a 'low-pass filter', i.e. if there is a strong attenuation of the system characteristics  $\phi(j\omega)$  outside a narrow frequency range. In a feedback configuration, i.e. when a process is controlled by means of a feedback control loop, the low-pass filtering effect is more pronounced than in an open-loop configuration and the distortion problem can easily be minimized. In summary, to maximize the reliability of the equivalent gain approach it should be applied in the case of non-stationary random perturbations with modest variations in the input amplitude.

Dual perturbations can be readily handled via the equivalent gain concept as mentioned in Section 2. If  $p_1(x_1)$  and  $p_2(x_2)$  represent the APD of perturbations in the flow rate and in the electric current, respectively, then Equation 6 is the joint APD of the two input perturbations and Equation 7 is the equivalent gain of the tank electrolyser. The  $f(r)$  relationship is the mathematical representation of the response of exit electrolyte concentration to simultaneous perturbations in flow rate and electric current. If both perturbations are Gaussian, the equivalent gain is given by Equation 8; as in the single input case the analysis can be carried out under on-line plant conditions without interrupting normal operations. A similar analysis can be applied to other perturbation pairs, e.g. to simultaneous perturbations in flow rate and inlet concentration.

In conclusion, the equivalent gain technique is one viable means of accounting for non-ideal behaviour of real-life tank electrolysers where the CSTER model may yield unsatisfactory results. Although the technique is well known in non-linear control theory it is a new concept in electrolytic



reaction engineering and the extent of its potential remains to be established. This paper provides a framework for its eventual utilization in this context.

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### Appendix 1. The derivation of Equation 12

Substituting Equation 11 into Equation 5, the relationship

$$K = \frac{m}{\sigma(2\pi)^{1/2}} \int_{-\infty}^{+\infty} |x|^{m-1} \exp(-x^2/2\sigma^2) dx = \frac{2m}{\sigma(2\pi)^{1/2}} \int_0^{+\infty} x^{(m-1)} \exp(-x^2/2\sigma^2) dx \quad (\text{A.1})$$

is obtained. Using the integral expression [27]

$$\int_0^{\infty} \exp(-qx^n) x^{np-1} dx = \frac{\Gamma(p)}{nq^p} \quad (\text{A.2})$$

where  $n$  is integer;  $p$  and  $q$  are fractions, Equation 12 is obtained on the necessary algebraic simplifications. By comparison  $n = 2$ ,  $q = 1/2\sigma^2$  and  $p = m/2$ . Numerical values of the gamma function defined as

$$\Gamma(x) \equiv \int_0^{\infty} t^{x-1} \exp(-t) dt \quad (\text{A.3})$$

are readily available in handbooks (e.g. [28]).

### Appendix 2. The derivation of Equation 14

As outlined by West [9], the substitution of Equation 13 into Equation 4a yields two integral expressions:

$$\begin{aligned} K &= \frac{1}{2\sigma^3(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \sum_{k=0}^n a_{2k} x^{2k} \exp(-x^2/2\sigma^2) d(x^2) \\ &+ \frac{1}{\sigma^3(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \sum_{k=0}^n a_{2k+1} x^{2k+2} \exp(-x^2/2\sigma^2) dx \end{aligned} \quad (\text{A.4})$$

of which the first one is zero. Thus, the equivalent gain is given by

$$K = \frac{2}{\sigma^3(2\pi)^{1/2}} \int_0^{\infty} \sum_{k=0}^n a_{2k+1} x^{2k+2} \exp(-x^2/2\sigma^2) dx \quad (\text{A.5})$$

Considering the general integral term

$$\frac{2}{\sigma^3(2\pi)^{1/2}} \int_0^{\infty} a_{2k+1} x^{2k+2} \exp(-x^2/2\sigma^2) dx$$

and taking into account the relationship [27]

$$\int_0^{\infty} x^{2n} \exp(-sx^2) dx = \frac{1.3.5 \dots (2n+1)}{2^{n+1} s^n} \left(\frac{\pi}{s}\right)^{1/2}; \quad s > 0 \quad (\text{A.6})$$

and using equivalences  $n = k + 1$  and  $s = 1/2\sigma^2$ , the general integral term is simplified to

$$\frac{2}{\sigma^3(2\pi)^{1/2}} \frac{1.3.5 \dots (2k+1) 2^{k+1} \sigma^{2k+2} \sigma(2\pi)^{1/2}}{2^{k+2}} = 1.3.5 \dots (2k+1) \sigma^{2k}$$

hence

$$K = \sum_{k=0}^n a_{2k+1}(1.3.5 \dots 2k + 1)\sigma^{2k}$$

which is Equation 14.

### Appendix 3. A short derivation of Equation 16

Consider a linear system with a steady-state frequency response  $K\phi(j\omega)$  and power spectral density  $\psi_x(\omega)$  for its input function  $x(t)$ . Then, the average input power into the system may be written as

$$\overline{x(t)^2} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \psi_x(\omega) d\omega \quad (\text{A.7})$$

The average output power of the system is given by the similar relationship

$$\overline{y(t)^2} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \psi_y(\omega) d\omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \psi_x(\omega) |K\phi(j\omega)|^2 d\omega$$

by applying the superposition theorem (or convolution theorem) of Fourier transforms to the input-output relationship. Thus

$$\psi_y(\omega) = \psi_x(\omega) |K\phi(j\omega)|^2 = K^2 |\phi(j\omega)|^2 \psi_x(\omega)$$

which is Equation 16. A detailed derivation may be found in Sections 3.8 and 3.9 of [9].

### References

- [1] D. J. Pickett, 'Electrochemical Reactor Design', Elsevier, Amsterdam (1977) 1979.
- [2] D. T. Chin and C. Y. Cheng, in 'Techniques of Electroorganic Synthesis', Part III (edited by N. L. Weinberg and B. V. Tilak), Wiley, New York (1982) chap. 1.
- [3] F. Coeuret and A. Storck, 'Elements de Génie Electrochimique', Lavoisier, Paris (1984).
- [4] T. Z. Fahidy, 'Principles of Electrochemical Reactor Analysis', Elsevier, Amsterdam (1985).
- [5] O. Levenspiel, 'Chemical Reaction Engineering', Wiley, New York (1972).
- [6] J. M. Smith, 'Chemical Engineering Kinetics', McGraw Hill, New York (1970).
- [7] V. V. Solodovnikov, 'Introduction to the Statistical Dynamics of Automatic Control Systems', Dover, New York (1960).
- [8] A. A. Pervozvanskii, 'Random Processes in Nonlinear Control Systems', Academic Press, New York (1965).
- [9] J. C. West, 'Analytical Techniques for Nonlinear Control Systems', Van Nostrand, New York (1960).
- [10] D. Graham and D. McRuer, 'Analysis of Nonlinear Control Systems', Dover, New York (1961).
- [11] Y. Sawaragi, N. Sugai and Y. Sunahara, 'Statistical Studies of Nonlinear Control Systems', Nippon Printing and Publishing Co. Osaka (1962).
- [12] F. H. Lange, 'Correlation Techniques', Van Nostrand Reinhold, New York (1966).
- [13] D. Graupe, 'Identification of Systems', Van Nostrand Reinhold, New York (1972).
- [14] Yu. E. Gushchin, *Telecomm. Radio Eng.* **33-34** (1979) 115.
- [15] G. H. Hostetter, *Proc. IEEE* **68** (1980) 284.
- [16] A. Blunden, D. C. O'Prey and W. H. Tait, *Nucl. Instrum. Methods Phys. Res.* **216** (1983) 191.
- [17] L. Marple, *IEEE Trans. Acoust. Speech Signal Process.* ASSP-28 (1980) 441.
- [18] M. E. Korobkov, *J. Appl. Spectrosc.* **25** (1976) 920.
- [19] J. C. Burgess, *J. Acoust. Soc. Amer.* **58** (1975) 556.
- [20] E. B. Arnold, *Nucl. Instrum. Methods* **125** (1975) 391.
- [21] M. Celasco, *J. Appl. Phys.* **48** (1977) 3635.
- [22] Y. Yoshida, *Electron. Commun. Jap.* **56** (1973) 64.
- [23] G. C. Carter and A. H. Nuttel, *Signal Process.* **2** (1980) 387.
- [24] D. Halford, J. H. Shoaf and A. S. Rislely, *Symp. Freq. Control 27th Ann. Proc. Pap. Cherry Hill (New Jersey)*, June 12-14 (1973), 421 (EIA, Washington, DC).
- [25] C. Lakshmi-Bai, *AIEE Trans. Part II* **79** (1960) 249.
- [26] R. E. Walpole, 'Introduction to Statistics', 3rd edn, Macmillan, New York (1982).
- [27] I. S. Gradshteyn and I. M. Ryzhik, 'Table of Integrals, Series and Products', Academic Press, New York (1980).
- [28] M. Abramowitz and I. A. Stegun, 'Handbook of Mathematical Functions', Dover, New York (1972).