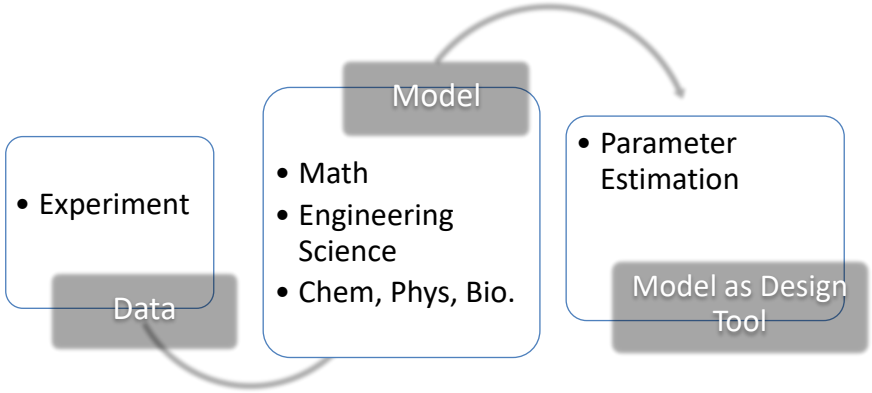
# Applications of Optimization:

# Parameter Estimation for Chemical and Biological Engineering Models[1]

## Models and parameter estimation




- Models contain Adjustable Parameters that need to be estimated by matching the model with data. WHY?
- **Parameter estimation** or **nonlinear regression** is the process of obtaining values of the parameters from matching of the model-based calculated values to the set of measurements (data)

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**Note:** If the model is an empirical (black box) we have no *a priori* information about the form of the model or any parameters. The problem of constructing a model purely from input/output data is called *identification problem*[2].

[1] Englezos, P., and N.E. Kalogerakis, Applied Parameter Estimation for Chemical Engineers, Marcel-Dekker, 2001

[2] Seinfeld, J.S., and L. Lapidus, Mathematical Models in Chemical Engineering, Vol. 3, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1974.

**Introduction**[3]. During an experiment, measurement of certain variables e.g. concentrations, pressures, temperatures, etc. is conducted.

Let $\hat{\mathbf{y}} = [\hat{y}_1, \hat{y}_2, ..., \hat{y}_m]^T$ be the *m-dimensional* vector of measured variables during an experiment. In addition, during each experiment, certain conditions are set or fixed by the experimentalist e.g. substrate concentration in an enzyme kinetics experiment, time and temperature in a kinetics experiment, etc. Let $\mathbf{x} = [x_1, x_2, ..., x_n]^T$ be the *n-dimensional* vector of these input variables that can be assumed to be known precisely.

> The experimentalist often formulates a mathematical model based on conservation equations and transport phenomena principles in order to describe the observed behavior. In general, the model consists of a set of equations based on the principles of chemistry, physics, thermodynamics, kinetics and transport phenomena and attempts to predict the variables, **y**, that are being measured.

In general, the measured variables **y** are a function of **x.** Thus, the model has the following form

$$\hat{\mathbf{y}} = \textit{Function of } (\mathbf{x}, \mathbf{k}) + \textit{Random Error} \qquad (1.1)$$

The random error arises from the measurement of y the true value of which is not known. The measurements are assumed to be free of systematic errors[4]. The modeling equations contain *adjustable parameters*. For example, kinetic rate expressions contain rate constants (parameters) the value of which is unknown and not possible to be obtained from fundamental principles. Let $\mathbf{k} = [k_1, k_2, \ldots, k_p]^T$ be the *p-dimensional* vector of parameters

*Parameter estimation* refers to the process of obtaining values of the parameters from the matching of the model-based calculated values to the set of measurements (data). This is the classic *parameter estimation* or *model fitting* problem and it should be distinguished from the *identification* problem. The latter involves the development of a model from input/output data only. This case arises when there is no a priori information about the form of the model i.e. it is a black box.

When the model equations are linear functions of the parameters the problem is called *linear estimation*. *Nonlinear estimation* refers to the most frequently encountered situation where the model equations are nonlinear functions of the parameters. Our focus will be on the estimation of adjustable parameters in nonlinear models described by algebraic or ordinary differential equations.

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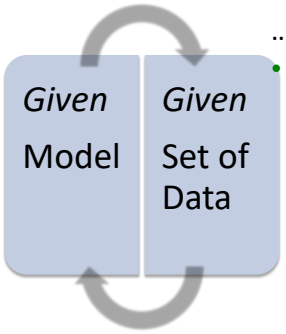
[3] Englezos, P., and N.E. Kalogerakis, Applied Parameter Estimation for Chemical Engineers, Marcel-Dekker, 2001

[4] SEE Appendix for an aside on Errors

The unknown model parameters will be obtained by minimizing a suitable *objective function*. The objective function is a measure of the discrepancy or the departure of the data from the model i.e., the *lack of fit*. Thus, this is an optimization problem. Note that engineers use the term *parameter estimation* whereas statisticians use such terms as *nonlinear* or *linear regression analysis* to describe this subject.

How do we apply parameter estimation?

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- *Minimize* $S(\mathbf{k})$

$$S(\mathbf{k}) = \sum_{i=1}^{N} \left[ \hat{\mathbf{y}}_i - f(\mathbf{x}, \mathbf{k}) \right]^2$$

  - where **k** is vector of estimated parameters

In parameter estimation, the general problem we have to solve is:

*Given the structure of the model* (*i.e. the governing model equations*) *and a set of measured data points, the problem is to find the unknown model parameters so that the values calculated by the model match the data in some optimal manner* (*e.g., by minimizing the sum of squares of errors*)

The specific issues that we have tried to address are:

*(i)* *Structure of the Model* ("What kind of models can be used? Linear or nonlinear? Algebraic or differential equation models?")

*(ii)* Selection of the *Objective Function* ("What do we minimize to estimate the parameters?")

*(iii)* *Solution Techniques* ("How do we minimize the objective function?")

*(iv)* *Statistical Properties of Parameter Estimates* ("How accurate are the estimated parameters?")

*(v)* *Statistical Properties of Model-Based Calculated Values* ("Given the uncertainty in the model parameters, what is the uncertainty in the calculated values?")

*(vi)* *Tests for Model Adequacy* ("Is the model good enough?")

*(vii)* *Tests for Model Discrimination* ("Among several rival models, which is the best one?")

*(viii)* *Factorial Experimental Design* ("What is the first set of experiments I should run?")

*(ix)* *Sequential Experimental Design* ("What should my next experiment be so that I gather maximum information?") for *model discrimination* (to select the best model among several ones that fit the data,) or for *precise parameter estimation* (to minimize further the parameter uncertainty in a particular model).

**Formulation of the Parameter Estimation Problem[5].** In the formulation of the parameter estimation problem we must answer two questions: (a) *what type of mathematical model do we have*? (b) *what type of objective function should we minimize*? Here we address both these questions. Our primary focus is the treatment of mathematical models that are nonlinear with respect to the parameters (*nonlinear regression*). Consideration to linear models (*linear regression*) will also be given.

## STRUCTURE OF THE MATHEMATICAL MODEL

The primary classification that is employed throughout this book is *algebraic* versus *differential* equation models. Namely, the mathematical model is comprised of a set of algebraic equations or by a set of ordinary (ODE) or partial differential equations (PDE). The majority of mathematical models for physical or engineered systems can be classified in one of these two categories.

**ALGEBRAIC EQUATION MODELS**. Let us consider a batch reactor where the following consecutive reactions take place (Smith, 1981)

$$A \xrightarrow{k_1} B \xrightarrow{k_2} D \qquad (4.12)$$

KINETICS[6]: $dC_A/dt = -k_1C_A$, $dC_B/dt=k_1C_A-K_2C_B$, $dC_D/dt=k_2C_B$

Because of the concentration invariant $C_A+C_B+C_D= C_{A0}$, i.e. that there is no change in the total number of moles, the integrated forms of the *isothermal rate equations* are

$$C_A(t) = C_{A0}e^{-k_1t} \qquad (4.13a)$$

$$C_B(t) = C_{A0}k_1\left(\frac{e^{-k_1t}}{k_2-k_1}+\frac{e^{-k_2t}}{k_2-k_1}\right) \qquad (4.13b)$$

$$C_D(t) = C_{A0} - C_A(t) - C_B(t) \qquad (4.13c)$$

where $C_A$, $C_B$ and $C_D$ are the concentrations of A, B and D respectively, t is the reaction time, and $k_1$, $k_2$ are the unknown rate constants.

During a typical experiment, the concentrations of A and B are only measured as a function of time. Namely, a typical dataset is of the form $[t_i, C_{Ai}, C_{Bi}]$, i=1,…,N.

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[5] Englezos, P. and N. Kalogerakis, "*Applied Parameter Estimation for Chemical Engineers*", Marcel-Dekker, New York, 2001

[6] Smith, J.M., Chemical Engineering kinetics, 1981, McGraw Hill.

The variables, the parameters and the governing equations for this problem can be re-written as follows:

| | | |
|---|---|---|
| Parameter vector: | $\mathbf{k} = [k_1, k_2]^T$ | |
| Vector of independent variables (also called regressor or input variables) | $\mathbf{x} = [x_1]$ | where $x_1 = t$ |
| Output vector (dependent variables) (also called output variables): | $\mathbf{y} = [y_1, y_2]^T$ | where $y_1 = C_A$, $y_2 = C_B$ |
| Model equations (vector function of known form): | $\mathbf{f} = [f_1, f_2]^T$ | |

where

$$f_1(x_1, k_1, k_2) = C_{A0} e^{-k_1 x_1} \tag{4.14a}$$

$$f_2(x_1, k_1, k_2) = C_{A0} k_1 \left( \frac{e^{-k_1 x_1}}{k_2 - k_1} + \frac{e^{-k_2 x_1}}{k_2 - k_1} \right) \tag{4.14b}$$

Thus, algebraic equation models are of the form. $\mathbf{y} = \mathbf{f}(\mathbf{x}, \mathbf{k})$ (2.1)
where

$\mathbf{k} = [k_1, k_2, \ldots, k_p]^T$ is a *p-dimensional* vector of parameters

$\mathbf{x} = [x_1, x_2, \ldots, x_n]^T$ is an *n-dimensional* vector of *independent* variables (also called *regressor* or *input* variables) which are either fixed for each experiment or which are measured;

$\mathbf{y} = [y_1, y_2, \ldots, y_m]^T$ is an *m-dimensional* vector of *dependent* variables (also often described as *response* variables or the *output* vector); these are the model variables which are actually measured;

$\mathbf{f} = [f_1, f_2, \ldots, f_m]^T$ is an *m-dimensional* vector function of known form (these are the actual model equations).

The **general form of the model** [$\mathbf{y} = \mathbf{f}(\mathbf{x}, \mathbf{k})$] is the *multi-response* with several independent variables model (i.e., $m>1$, $n>1$)

$$\begin{bmatrix} y_1 \\ y_2 \\ . \\ . \\ . \\ y_m \end{bmatrix} = \begin{bmatrix} f_1(x_1,x_2,...,x_n;k_1,k_2,...,k_p) \\ f_2(x_1,x_2,...,x_n;k_1,k_2,...,k_p) \\ . \\ . \\ . \\ f_m(x_1,x_2,...,x_n;k_1,k_2,...,k_p) \end{bmatrix} \quad (2.2c)$$

A single experiment consists of the measurement of each of the $m$ response variables for a given set of values of the $n$ independent variables. For each experiment, the measured output vector which can be viewed as a random variable is comprised of the deterministic part calculated by the model (Eqn 2.1) and the stochastic part represented by the error term, i.e

$$\hat{\mathbf{y}}_i = \mathbf{f}(\mathbf{x}_i, \mathbf{k}) + \boldsymbol{\varepsilon}_i \quad ; \quad i=1,2,\ldots,N \qquad (2.3)$$

If the mathematical model represents adequately the physical system, the error term in Equation 2.3 represents only measurement errors. As such, it can often be assumed to be normally distributed with zero mean (assuming there is no bias present in the measurement). In real life the vector $\boldsymbol{\varepsilon}$, incorporates not only the experimental error but also any inaccuracy of the mathematical model.

***Example*: Catalytic Reduction of Nitric Oxide by $H_2$**[7]

$$NO + H_2 \longleftrightarrow H_2O + \frac{1}{2}N_2 \qquad (4.29)$$

Data were taken at 375, 400 ℃, and 425 ℃ using $N_2$ as the diluent and given in Table 4.5. The reaction rate in *gmol/(min·g-catalyst)* and the total NO conversion were measured at different partial pressures for $H_2$ and NO. A *Langmuir-Hinshelwood reaction rate model* for the reaction between an adsorbed NO molecule and one $H_2$ molecule is described by:

$$r = \frac{kK_{H_2}K_{NO}p_{H_2}p_{NO}}{\left(1 + K_{NO}p_{NO} + K_{H_2}p_{H_2}\right)^2} \qquad (4.30)$$

where r is the reaction rate in *gmol/(min·g-catalyst)*, $p_{H2}$ is the partial pressure of hydrogen (*atm*), $p_{NO}$ is the partial pressure of NO (*atm*), $K_{NO}$ ($atm^{-1}$) is the adsorption equilibrium constant for NO, $K_{H2}$ ($atm^{-1}$) is the adsorption equilibrium constant for $H_2$ and k is the forward reaction rate constant for surface reaction.

Using our standard notation:

| | | |
|---|---|---|
| Parameter vector: | $\mathbf{k} = [k_1, k_2, k_3]^T$ | where $k_1=k$, $k_2=K_{H2}$ & $k_3=K_{NO}$ |
| Independent variables | $\mathbf{x} = [x_1, x_2]^T$ | where $x_1=p_{H2}$, $x_2=p_{NO}$ |
| Output vector | $\mathbf{y} = [y_1]$ | where $y_1=r$ |
| Model Equation | $\mathbf{f} = [f_1]$ | |

where $$f_1(x_1, x_2, k_1, k_2, k_3) = \frac{k_1 k_2 k_3 x_1 x_2}{\left(1 + k_3 x_2 + k_2 x_1\right)^2} \qquad (4.31)$$

**Linear Models.** A special case of Equation 2.3 corresponds to the celebrated *linear systems*. Linearity is assumed with respect to the unknown parameters rather than the independent variables. Hence, Equation 2.3 becomes

$$\hat{\mathbf{y}}_i = \mathbf{F}(\mathbf{x}_i)\mathbf{k} + \boldsymbol{\varepsilon}_i \quad ; \quad i=1,2,\ldots,N \qquad (2.4)$$

where $\mathbf{F}(\mathbf{x}_i)$ is an *m×p dimensional* matrix which depends only on $\mathbf{x}_i$ and it is independent of the parameters. Quite often the elements of matrix **F** are simply the independent variables ➔ the well known *linear regression* model,

$$\hat{\mathbf{y}}_i = \mathbf{X}_i\,\mathbf{k} + \boldsymbol{\varepsilon}_i \quad ; \quad i=1,2,\ldots,N \qquad (2.5)$$

[7] Ayen and Peters, *Ind Eng Chem Proc Des Dev.*, 1, 204-207, 1962

**DIFFERENTIAL EQUATION MODELS**. In general, the model equations can be written in the form

$$\frac{d\mathbf{x}(t)}{dt} = \mathbf{f}(\mathbf{x}(t), \mathbf{u}, \mathbf{k}) \quad ; \quad \mathbf{x}(t_0) = \mathbf{x}_0 \qquad (2.10)$$

$$\mathbf{y}(t) = \mathbf{C}\mathbf{x}(t) \qquad (2.11)$$

where

$\mathbf{k}=[k_1,k_2,\ldots,k_p]^T$ is a *p-dimensional* vector of parameters whose numerical values are unknown;

$\mathbf{x}=[x_1,x_2,\ldots,x_n]^T$ is an *n-dimensional* vector of state variables;

$\mathbf{x}_0=[x_{10},x_{20},\ldots,x_{n0}]^T$ is an *n-dimensional* vector of initial conditions assumed to be known precisely

$\mathbf{u}=[u_1,u_2,\ldots,u_r]^T$ is an *r-dimensional* vector of manipulated variables which are either set by the experimentalist and their values are precisely known or they have been measured;

$\mathbf{f}=[f_1,f_2,\ldots,f_n]^T$ is a *n-dimensional* vector function of known form (the differential equations);

$\mathbf{C}$ is the $m \times n$ observation matrix which indicates the state variables that are measured

$\mathbf{y}=[y_1,y_2,\ldots,y_m]^T$ is the *m-dimensional* output vector i.e., the set of variables that are measured experimentally

The measured output vector at time $t_i$, denoted as $\hat{\mathbf{y}}_i$, is related to the value calculated by the model through the error term,

$$\hat{\mathbf{y}}_i = \mathbf{y}(t_i) + \boldsymbol{\varepsilon}_i \quad ; \quad i=1,2,\ldots,N \qquad (2.13)$$

## EXAMPLE: A Homogeneous Gas Phase Reaction

Estimate the two rate constants $k_1$ and $k_2$ in the Bodenstein-Linder model for the homogeneous gas phase reaction of NO with $O_2$:

$$2NO + O_2 \longleftrightarrow 2NO_2$$

The model is described by the following equation

$$\frac{dx}{dt} = k_1(\alpha - x)(\beta - x)^2 - k_2 x^2 \quad ; \quad x(0) = 0 \qquad (6.45)$$

where $\alpha$=126.2, $\beta$=91.9 and x is the concentration of $NO_2$.
The concentration of $NO_2$ was measured as a function of time and the data are given in Table 6.1

The model is of the form $dx/dt=f(x,k_1,k_2)$
where $f(x,k_1,k_2)=k_1(\alpha-x)(\beta-x)^2-k_2x^2$.
The single state variable x is also the measured variable (i.e., y(t)=x(t)).

*Table 6.1 Data for the Homogeneous Gas Phase Reaction of NO with $O_2$.*

| *Time* | *Concentration of $NO_2$* |
|---|---|
| 0 | 0 |
| 1 | 1.4 |
| 2 | 6.3 |
| 3 | 10.5 |
| 4 | 14.2 |
| 5 | 17.6 |
| 6 | 21.4 |
| 7 | 23.0 |
| 9 | 27.0 |
| 11 | 30.5 |
| 14 | 34.4 |
| 19 | 38.8 |
| 24 | 41.6 |
| 29 | 43.5 |
| 39 | 45.3 |

*Source:* Bellman et al. (1967).

# THE OBJECTIVE FUNCTION OR PERFORMANCE INDEX

The *objective function*, S(**k**), is a suitable measure of the *overall* departure of the model-calculated values from the measurements

(residual $\mathbf{e}_i$) $$\mathbf{e}_i = \left[\hat{\mathbf{y}}_i - \mathbf{f}\left(\mathbf{x}_i, \mathbf{k}\right)\right] \qquad (2.14)$$

where the model-based value $\mathbf{f}(\mathbf{x}_i,\mathbf{k})$ is calculated using the *estimated parameter values*.

It should be noted that the residual ($\mathbf{e}_i$) is not the same as the error term ($\boldsymbol{\varepsilon}_i$) in Equation 2.13.

$$\hat{\mathbf{y}}_i = \mathbf{y}(t_i) + \boldsymbol{\varepsilon}_i \quad ; \quad i=1,2,\ldots,N \qquad (2.13)$$

The error term ($\boldsymbol{\varepsilon}_i$) corresponds to the true parameter values that are never known exactly, whereas the residual ($\mathbf{e}_i$) corresponds to the estimated parameter values.

Given N measurements of the output vector, the parameters can be obtained by minimizing the *Least Squares* (LS) objective function which is given below as the *weighted sum of squares of the residuals*, namely,

$$S_{LS}(\mathbf{k}) = \sum_{i=1}^{N} \mathbf{e}_i^T \mathbf{Q}_i \mathbf{e}_i \qquad (2.15a)$$

where $\mathbf{e}_i$ is the vector of residuals from the $i^{th}$ experiment.

The LS objective function for *algebraic systems* takes the form,

$$S_{LS}(\mathbf{k}) = \sum_{i=1}^{N} \left[\hat{\mathbf{y}}_i - \mathbf{f}(\mathbf{x}_i,\mathbf{k})\right]^T \mathbf{Q}_i \left[\hat{\mathbf{y}}_i - \mathbf{f}(\mathbf{x}_i,\mathbf{k})\right] \qquad (2.15b)$$

For systems described by *ODEs*

$$S_{LS}(\mathbf{k}) = \sum_{i=1}^{N} \left[\hat{\mathbf{y}}_i - \mathbf{y}(t_i,\mathbf{k})\right]^T \mathbf{Q}_i \left[\hat{\mathbf{y}}_i - \mathbf{y}(t_i,\mathbf{k})\right] \qquad (2.15c)$$

Depending on our choice of the weighting matrix $Q_i$ in the objective function we have the following cases:

- **Unweighted Least Squares (LS) Estimation: $\mathbf{Q}_i=\mathbf{I}$**

$$S_{LS}(\mathbf{k}) = \sum_{i=1}^{N} \mathbf{e}_i^T \mathbf{e}_i \qquad (2.16)$$

- **Weighted Least Squares (WLS) Estimation: $\mathbf{Q}_i=\mathbf{Q}$** for all i=1,2,..,N

- **Generalized Least Squares (GLS) Estimation**

In this case we minimize a weighted SSE with non-constant weights. The user-supplied weighting matrices differ from experiment to experiment.

Of course, it is not at all clear how one should select the weighting matrices $\mathbf{Q}_i$, i=1,…,N, even for cases where a constant weighting matrix $\mathbf{Q}$ is used. Practical guidelines for the selection of $\mathbf{Q}$ can be derived from *Maximum Likelihood (ML)* considerations.

- **Maximum Likelihood (ML) Estimation**

The method of maximum likelihood is a widely used method of estimation that produces estimators with desirable properties[8]. We specify the probability distribution of the observed data as a function of the parameters $Pr(\mathbf{x}|\mathbf{k})$ , or more generally $f(\mathbf{x}|\mathbf{k})$, where $\mathbf{x}$ denotes the data and $\mathbf{k}$ denotes the parameters. This probability distribution is then viewed as a function of the parameters conditional on the data, and this is called the likelihood function $L(\mathbf{k}|\mathbf{x})$. *We need to find the values of the parameters that maximize this function; that is, given the underlying model, for what values of the parameters are these data most likely*? These are the maximum likelihood estimators (MLEs)

If the mathematical model of the process under consideration is adequate, it is very reasonable to assume that the measured responses from the $i^{th}$ experiment are normally distributed. In particular the joint probability density function conditional on the value of the parameters ($\mathbf{k}$ and $\mathbf{\Sigma}_i$) is of the form,

[8] MacKenzie et al., Occupancy Estimation and Modeling, 2nd ed, chapter 3: Fundamentals of Statistical Inference, Academic Press, 2018.

$$p(\hat{\mathbf{y}}_i \mid \mathbf{k},\boldsymbol{\Sigma}_i) \sim det(\boldsymbol{\Sigma}_i)^{-1/2}\, exp\left\{-\frac{\mathbf{e}_i^T\boldsymbol{\Sigma}_i^{-1}\mathbf{e}_i}{2}\right\} \qquad (2.17)$$

where $\boldsymbol{\Sigma}_i$ is the covariance matrix of the response variables $\mathbf{y}$ at the $i^{th}$ experiment and hence, of the residuals $\mathbf{e}_i$ too.

If we now further assume that measurements from *different experiments are independent*, the joint probability density function for the all the measured responses is simply the product,

$$p(\hat{\mathbf{y}}_1,\hat{\mathbf{y}}_2,\ldots,\hat{\mathbf{y}}_N \mid \mathbf{k}, \boldsymbol{\Sigma}_1,\boldsymbol{\Sigma}_2,\ldots,\boldsymbol{\Sigma}_N) \sim det(\boldsymbol{\Sigma}_1)^{-1/2}\, det(\boldsymbol{\Sigma}_2)^{-1/2}\ldots det(\boldsymbol{\Sigma}_N)^{-1/2}$$
$$\times\; exp\left\{-\frac{\mathbf{e}_1^T\boldsymbol{\Sigma}_1^{-1}\mathbf{e}_1}{2}\right\} exp\left\{-\frac{\mathbf{e}_2^T\boldsymbol{\Sigma}_2^{-1}\mathbf{e}_2}{2}\right\}\ldots exp\left\{-\frac{\mathbf{e}_N^T\boldsymbol{\Sigma}_N^{-1}\mathbf{e}_N}{2}\right\} \qquad (2.18)$$

grouping together similar terms we have,

$$p(\hat{\mathbf{y}}_1,\hat{\mathbf{y}}_2,\ldots,\hat{\mathbf{y}}_N \mid \mathbf{k}, \boldsymbol{\Sigma}_1,\boldsymbol{\Sigma}_2,\ldots,\boldsymbol{\Sigma}_N) \sim \left(\prod_{i=1}^{N} det(\boldsymbol{\Sigma}_i)\right)^{-\frac{1}{2}} exp\left\{-\frac{1}{2}\sum_{i=1}^{N}\mathbf{e}_i^T\boldsymbol{\Sigma}_i^{-1}\mathbf{e}_i\right\} \qquad (2.19)$$

The *Loglikelihood* function is the *log* of the joint probability density function and is regarded as a function of the parameters conditional on the observed responses. Hence, we have

$$L(\mathbf{k}, \boldsymbol{\Sigma}_1,\boldsymbol{\Sigma}_2,\ldots,\boldsymbol{\Sigma}_N \mid \hat{\mathbf{y}}_1,\hat{\mathbf{y}}_2,\ldots,\hat{\mathbf{y}}_N) = A - \frac{1}{2}\sum_{i=1}^{N} log(det(\boldsymbol{\Sigma}_i)) - \frac{1}{2}\sum_{i=1}^{N}\mathbf{e}_i^T\boldsymbol{\Sigma}_i^{-1}\mathbf{e}_i \qquad (2.20)$$

where A is a constant quantity. The maximum likelihood estimates of the unknown parameters are obtained by maximizing the *Loglikelihood* function. At this point let us assume that the covariance matrices ($\boldsymbol{\Sigma}_i$) of the measured responses (and hence of the error terms) during each experiment are *known* precisely. Obviously, in such a case the ML parameter estimates are obtained by minimizing the following objective function

$$S_{ML}(\mathbf{k}) = \sum_{i=1}^{N}\mathbf{e}_i^T\boldsymbol{\Sigma}_i^{-1}\mathbf{e}_i \qquad (2.21)$$

Therefore, on statistical grounds, if the error terms ($\boldsymbol{\varepsilon}_i$) are normally distributed with zero mean and with a *known covariance matrix*, then $\mathbf{Q}_i$ should be the inverse of this covariance matrix, i.e.,

$$\mathbf{Q}_i = [COV(\boldsymbol{\varepsilon}_i)]^{-1} = \boldsymbol{\Sigma}_i^{-1} \quad ; \quad i=1,2,\ldots,N \qquad (2.22)$$

However, the requirement of *exact* knowledge of all covariance matrices ($\boldsymbol{\Sigma}_i$, i=1,2,…,N) is rather unrealistic. Fortunately, in many situations of practical importance, we can make certain quite reasonable assumptions about the structure of $\boldsymbol{\Sigma}_i$ that allow us to obtain the ML estimates using Equation 2.21. This approach can actually aid us in establishing guidelines for the selection of the weighting matrices $\mathbf{Q}_i$ in least squares estimation.

*Case I*: Let us consider the stringent assumption that the error terms in each response variable and for each experiment ($\boldsymbol{\varepsilon}_{ij}$, i=1,…N; j=1,…,*m*) are all identically and independently distributed (i.i.d) normally with zero mean and variance, $\sigma_e^2$. Namely,

$$\boldsymbol{\Sigma}_i = \sigma_e^2 \, \mathbf{I} \quad ; \quad i=1,2,\ldots,N \qquad (2.23)$$

where $\mathbf{I}$ is the $m \times m$ identity matrix. Substitution of $\boldsymbol{\Sigma}_i$ into Equation 2.21 yields

$$S_{ML}(\mathbf{k}) = \frac{1}{\sigma_e^2} \sum_{i=1}^{N} \mathbf{e}_i^T \mathbf{e}_i \qquad (2.24)$$

Obviously, minimization of $S_{ML}(\mathbf{k})$ in the above equation does not require the prior knowledge of the common factor $\sigma_e^2$. Therefore, under these conditions the ML estimation is equivalent to simple LS estimation ($\mathbf{Q}_i=\mathbf{I}$).

*Case II*: Next let us consider the more realistic assumption that the variance of a particular response variable is constant from experiment to experiment; however, different response variables have different variances, i.e.,

$$\boldsymbol{\Sigma}_i = \begin{bmatrix} \sigma_{e_1}^2 & 0 & \cdots & 0 \\ 0 & \sigma_{e_2}^2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \sigma_{em}^2 \end{bmatrix} \; ; \; i=1,2,\ldots,N \qquad (2.25)$$

Although we may not know the elements of the diagonal matrix $\boldsymbol{\Sigma}_i$ given by Equation 2.25, *we assume that we do know their relative value*. Namely we assume that we know the following ratios ($v_i$, i=1,2,…,*m*),

$$v_1 = \frac{\sigma_{e1}^2}{\sigma^2} \qquad (2.26a)$$

$$v_2 = \frac{\sigma_{e_2}^2}{\sigma^2} \qquad (2.26b)$$

$$v_m = \frac{\sigma_{e_m}^2}{\sigma^2} \qquad (2.26c)$$

where $\sigma^2$ is an unknown scaling factor. Therefore $\boldsymbol{\Sigma}_i$ can be written as

$$\boldsymbol{\Sigma}_i = \sigma^2 \, diag(v_1, v_2,\ldots,v_m) \quad ; \quad i=1,2,\ldots,N \qquad (2.27)$$

Upon substitution of $\boldsymbol{\Sigma}_i$ into Equation 2.21 it becomes apparent that the ML parameter estimates are the same as the weighted LS estimates when the following weighting matrices are used,

$$\mathbf{Q}_i = \mathbf{Q} = diag(v_1^{-1}, v_2^{-1},\ldots,v_m^{-1}) \qquad (2.28)$$

If the variances in Equation 2.25 are totally unknown, the ML parameter estimates can only be obtained by the *determinant criterion* presented later.

*Case III*: Generalized LS estimation will yield ML estimates whenever the errors are distributed with variances that change from experiment to

experiment. Therefore, in this case our choice for $\mathbf{Q}_i$ should be $[COV(\boldsymbol{\varepsilon}_i)]^{-1}$ for i=1,…,N.

An interesting situation that arises often in engineering practice is when the errors have a *constant, yet unknown, percent error for each variable*, i.e.

$$\sigma^2_{eij} = \sigma^2 y^2_{ij} \quad ; \quad i=1,2,\ldots,N \quad \text{and} \quad j=1,2,\ldots,m \tag{2.29}$$

where $\sigma^2$ is an unknown scaling factor. Again, upon substitution of $\boldsymbol{\Sigma}_i$ into Equation 2.21 it is readily seen that the ML parameter estimates are the same as the generalized LS estimates when the following weighting matrices are used,

$$\mathbf{Q}_i = diag(y^{-2}_{i1}, y^{-2}_{i2}, \ldots, y^{-2}_{im}) \quad ; \quad i=1,2,\ldots,N \tag{2.30}$$

The above choice has the computational disadvantage that the weights are a function of the unknown parameters. If the magnitude of the errors is not excessive, we could use the measurements in the weighting matrix with equally good results, namely

$$\mathbf{Q}_i = diag(\hat{y}^{-2}_{i1}, \hat{y}^{-2}_{i2}, \ldots, \hat{y}^{-2}_{im}) \quad ; \quad i=1,2,\ldots,N \tag{2.31}$$

### 2.2.1.5 The Determinant Criterion

If the covariance matrices of the response variables are unknown, the maximum likelihood parameter estimates are obtained by maximizing the *Loglikelihood* function (Equation 2.20) over **k** and the unknown variances. Following the distributional assumptions of Box and Draper (1965),[9] i.e.,

[9] The Bayesian Estimation of Common Parameters from Several Responses

**The Bayesian Estimation of Common Parameters from Several Responses**

George E. P. Box, Norman R. Draper, *Biometrika*, Vol. 52, No. 3/4 (Dec., 1965), pp. 355-365

assuming that $\boldsymbol{\Sigma}_1=\boldsymbol{\Sigma}_2=\ldots=\boldsymbol{\Sigma}_N=\boldsymbol{\Sigma}$, it can be shown that the ML parameter estimates can be obtained by minimizing the determinant (Bard, 1974)

$$S_{det}(\mathbf{k}) = det\left(\sum_{i=1}^{N}\mathbf{e}_i\mathbf{e}_i^T\right) \qquad (2.32)$$

In addition, the corresponding estimate of the unknown covariance is

$$\hat{\boldsymbol{\Sigma}} = \frac{1}{N}\sum_{i=1}^{N}\mathbf{e}_i\mathbf{e}_i^T \qquad (2.33)$$

It is worthwhile noting that Box and Draper (1965) arrived at the same determinant criterion following a Bayesian argument and assuming that $\boldsymbol{\Sigma}$ is unknown and that the prior distribution of the parameters is noninformative.

The determinant criterion is very powerful and it should be used to refine the parameter estimates obtained with least squares estimation if our assumptions about the covariance matrix are suspect.

### 2.2.1.6 Incorporation of Prior Information About the Parameters

Any prior information that is available about the parameter values can facilitate the estimation of the parameter values. The methodology to incorporate such information in the estimation procedure and the resulting benefits are discussed later.

# ERRORS

## It is impossible to measure physical quantities without errors

- **Error** (by Webster) is "*the difference between an observed or calculated value and the true value*".
- Usually we do not know the "true value" (That is why do the experiment!)



## Three categories of errors

- be careful and double check.
- (e.g. selecting data that suit your purpose)➔***scientific crime***

- e.g.faulty calibration of equipment, impurities in materials or from causes you do not know!
- Plan well to understand and reduce sources of such errors

- Fluctuations in observations
- Repeated experimentation ➔ *yields precise results*
- Use more reliable and more precise instruments (more $)

H. J.C. Berendsen, " A student's Guide to Data and Error Analysis", Cambridge Univ Press, 2011

## A systematic error can be a constant offset over the entire range of values, but *bias* can also be complex.

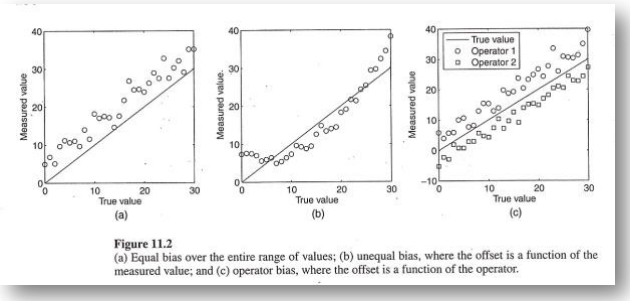


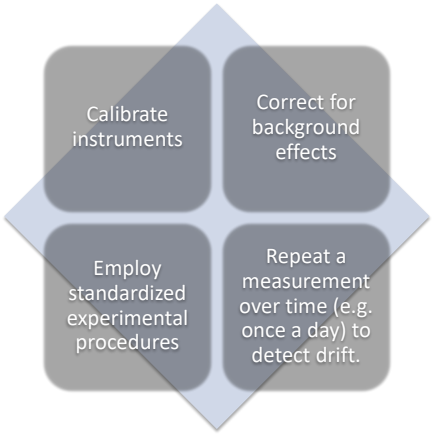

**Figure 11.2**
(a) Equal bias over the entire range of values; (b) unequal bias, where the offset is a function of the measured value; and (c) operator bias, where the offset is a function of the operator.

- Systematic error means that each repeated measurement at a certain condition is affected by the same influence. This situation is not improved by repeated measurements. Such error results in *bias* and is coupled to the measurement accuracy.
- Drift is also a cause for bias; for example, if parts of an instrument become worn with time.

O. Andersson, *Experiment,* Wiley, 2012.

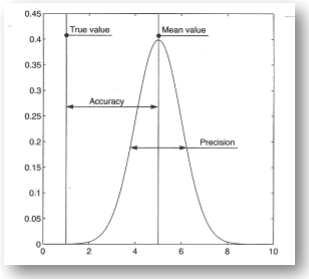


## Systematic errors must be handled differently than random errors



# **Random errors** or **Uncertainties**

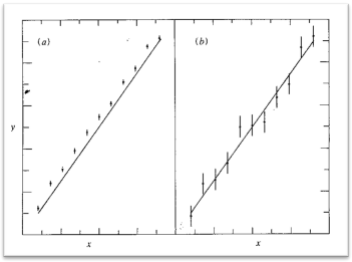
- Random errors are unavoidable and unpredictable ➔ the term "Uncertainty" is preferable.
- If a measurement is repeated many times the results show a certain *spread* around an average value➔ *Bell Curve*
  - The measured values are *random samples from a* probability distribution ➔






## It is important to distinguish between the terms **accuracy** and **precision**

- **Accuracy** of an experiment is a measure of how close the result of the experiment is to the true value
- **Precision** of an experiment is a measure of how well the result has been determined, without reference to its agreement with the true value.

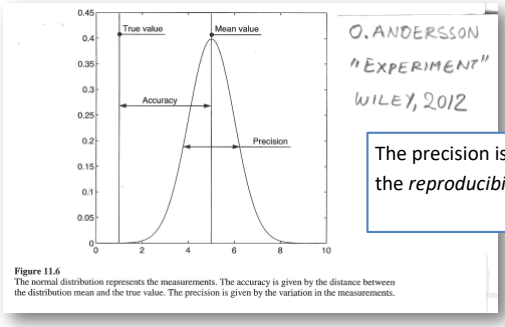



(a) Precise but inaccurate data
(b) Accurate but imprecise data
True values are represented by the Straight line.

P.R. Bevington and D.K. Robinson, "Data Reduction and Error Analysis for the Physical Sciences", 2nd ed, McGraw Hill, 1992.



## More on Accuracy vs. Precision




The precision is a measure of the *reproducibility* of the result

- Increasing the sample size may increase precision in the measured value but has no effect on the accuracy.
- Determining accuracy involves comparisons. For example, the accuracy of measuring the concentration of a substance is obtained by measuring a sample of known concentration. The offset between the measured value and the true value is a measure of the accuracy.