— COMPUTATIONAL RESULTS —
HOW RELIABLE ARE THEY?
A Systematic Approach to Model Validation

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Two recent papers in this journal[1,2] have discussed the ever-increasing role of computers in chemical engineering education and practice. While computers are heavily used for word processing and communication, their most noticeable effect in engineering education is their role as mathematical modeling and numerical computation tools.

The range of numerical computational tools available to the student and the practicing engineer includes spreadsheets for simple calculations, numerical computation packages such as MATLAB, MATHEMATICA, MAPLE, and POLYMATH, and powerful, sophisticated steady-state and dynamic simulation programs such as ASPEN, HYSIM, PROII, and SPEEDUP. These tools have considerably reduced the time and effort required for engineering calculations. They also make it possible to simulate operation of a complete process or even a plant. The sophisticated computational tools have not reduced, however, the need to verify and validate the results. Actually, there is probably more need than ever for verification of the results because some of the computational tools are used as a "black box" where the applied mathematical model is invisible to the user.

Most commercial simulation programs use the black-box approach where the user has to provide only a minimum amount of input data to specify the process. The mathematical model, the solution algorithm, and the physical and thermodynamic properties are provided by the program, and the user usually receives only the final results. This approach saves much of the user's time, but it makes it impossible to use some of the traditional methods for model validation and verification.

Himmelblau[3] quotes Finger and Naylor's[4] steps for model validation as: validation of the logic, validation of model behavior, and validation of model assumptions. Clearly, when the model is invisible to the user, neither its logic nor its simplifying assumptions can be validated. The user can only rely on the final results for validating the model.

Validating the model and verifying the results is more an art than a science, as Himmelblau notes. The model can never be completely validated because there are only finite number of tests that can be carried out,[5] and passing a certain number of tests does not ensure that the model is correct. In order to minimize the chance for errors, a verification process that uses the final results only as a diagnostic tool should be devised; this process should be used consistently, without taking anything for granted. The use of sophisticated computational tools can save a lot of time, but some of this saved time must be used for validation and verification of the results.

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In this paper, a model validation and verification process, based only on the final computational results, is presented and its use is demonstrated using several examples from the literature. We recommend that students be introduced to model validation toward the last quarter of a modeling and simulation course. The examples included in the paper can be best given as homework assignments where the student can use a numerical computation package (such as POLYMATH, MATLAB, or MATHEMATICA) to solve the problem and use the validation procedure to detect what is wrong with the solution. Some of the examples involve solution of stiff ordinary differential equations, and it is important to ensure that the software used by the students is capable of solving such equations.

Most of the readers have probably come across examples (even in research work) where the lack of model validation has led to embarrassing glitches. The examples we present are fairly simple, so that they can be easily understood by undergraduate students, do not require excessive amount of time for preparation, and can be solved using widely available software packages.

MODEL VALIDATION AND VERIFICATION PROCEDURE

The following procedure assumes that the only information available about the model is the final result.

1. *Solve a problem similar to the one you want to solve, but where the results can be verified using: process data, results from the literature, an analytical solution, or limiting cases (a typical example would be checking the steady-state solution for a dynamic problem). Compare the solution obtained by using the model with the results or data obtained independently.*

2. *Always investigate error messages and warnings that your program issues.*

3. *Check the results obtained for physical feasibility.*

4. *Carry out a sensitivity analysis by introducing small changes in the input data and user-selectable or adjustable parameters of the computer program (such as solution algorithm, error tolerance, plot interval, etc.). Look out for any unreasonable changes in the results caused by these parameter variations.*

While complete verification of the results is practically impossible, consistently carrying out the above four steps of verification can prevent most of the common errors encountered in simulation and numerical computation. Some examples that demonstrate this procedure follow.

— Example 1 —

Transient Behavior of a Catalytic Fluidized Bed

Luss and Amundson[6] studied a simplified model for the dynamics of a catalytic fluidized bed in which an irreversible gas phase reaction $A \rightarrow B$ is assumed to occur. The mass and energy conservation equations for this system were

$$\frac{dP}{d\tau} = P_e - P + H_g\left(P_p - P\right) \tag{1a}$$

$$\frac{dT}{d\tau} = T_e - T + H_T\left(T_p - T\right) + H_w\left(T_w - T\right) \tag{1b}$$

$$\frac{dP_p}{d\tau} = \frac{H_g}{A}\left[P - P_p(1+k)\right] \tag{1c}$$

$$\frac{dT_p}{d\tau} = \frac{H_T}{C}\left[\left(T - T_p\right) + FkP_p\right] \tag{1d}$$

where

$$k = 0.0006 \exp(20.7 - 15000/T_p)$$

$T^\circ(R), P(atm) = $ temperature and partial pressure of the reactant in the fluid

$T_p(^\circ R), P_p(atm) = $ temperature and partial pressure of the reactant at the catalyst

$\tau = $ dimensionless time

$H_g, H_T, F, A, C = $ dimensionless constants

and the subscript e indicates entrance conditions. The following numerical values were provided by Luss and Amundson:

$P_e = 0.1$ atm $C = 205.74$ $H_g = 320$

$T_e = 600^\circ R$ $F = 8000$ $H_T = 266.667$ $A = 0.17142$

Luss and Amundson noted that the system of ordinary differential equations (ODE) representing the catalytic fluidized bed is a stiff system. At that time, there were no established methods for solving stiff systems of ODEs and they derived a special technique to solve it.

Subsequently, Aiken and Lapidus[7] proposed a different method for solving stiff ODEs. They used the system of Eq. (1) as a test example, but rewrote the system of equations by introducing the numerical values into system (1) and rounding some of the coefficient as follows:

$$\frac{dP}{d\tau} = 0.1 + 320 P_p - 321 P \tag{2a}$$

$$\frac{dT}{d\tau} = 1752 - 269 T + 267 T_p \tag{2b}$$

$$\frac{dP_p}{d\tau} = 1.88 \times 10^3\left[P - P_p(1+k)\right] \tag{2c}$$

$$\frac{dT_p}{d\tau} = 1.3\left(T - T_p\right) + 1.04 \times 10^4 \, kP_p \tag{2d}$$

One possible assignment for the students in this example can be to verify that Eq. (1) and Eq. (2) yield the same steady-state solutions.

Luss and Amundson have identified three steady-state solutions for this problem. The values of P, P_p, T, and T_p at the three steady states reported by Luss and Amundson are shown in Table 1.

To find the steady-state solutions, the time derivatives in the four equations of systems (1) and (2) are set equal to zero. The systems can then be reformulated to give a single implicit nonlinear equation, which should equal to zero, while the rest of the variables can be calculated from explicit expressions. Introducing the numerical values of the constants into Eq. (1) and reformulating yields

$$f(T) = 1.296\left(T - T_p\right) + 10369\, kP_p \tag{3a}$$

$$T_p = (269.267\, T - 1752) / 266.667 \tag{3b}$$

$$P_p = -0.1 / \left\{ 321\left[320 / 321 - (1 + k)\right] \right\} \tag{3c}$$

$$P = \frac{\left(320\, P_p + 0.1\right)}{321} \tag{3d}$$

System (2) can be written in a similar manner. Figure 1 displays plots of f(T) versus T in the region $500°R \le T \le 1300°R$ using both the original and revised formulations. It can be seen that the original formulation yields three steady states at the points indicated by Luss and Amundson, whereas the revised formulation gives only a single root at T = 1210.8.

Thus, when there is very little difference between the

TABLE 1
Steady-State Solutions
of the Catalytic Fluidized Bed[6]

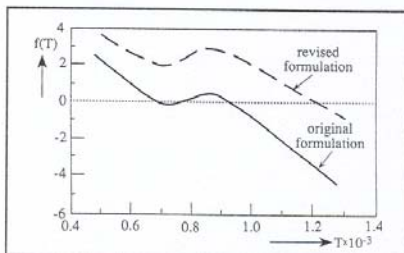| | Steady States | | |
	First	Second	Third
p(atm)	0.09352	0.06704	0.006822
P_p(atm)	0.09350	0.06694	0.006531
T(°R)	690.445	753.344	912.764
T_p(°R)	690.607	759.167	915.094

Figure 1. *Steady states of the catalytic fluidized bed reactor using original and revised model formulations.*

original (Eq. 1) and revised (Eq. 2) formulation, they actually do represent a much different problem. The discrepancy between the original and revised formulation was detected by Michelsen[9] two years after the revised formulation was published. In the meantime, this formulation was extensively used for testing software (see, for example, reference 8) without noticing that it actually was a different problem. To understand the reason for this difference, the expression for T_p in Eq. (3b) can be introduced into Eq. (3a) to yield

$$f(T) = 8.5147 - 0.0126\, T + 10369\, kP_p \tag{4}$$

Carrying out the same substitution using the modified formulation yields

$$f(T) = 8.53 - 0.00974\, T + 1.04 \times 10^4\, kP_p \tag{5}$$

It can be seen that the coefficients of T in Eqs. (4) and (5) are significantly different, thus rounding the numbers at the third decimal digit in Eq. (2b) resulted in not even one correct digit in the coefficient of T in Eq. (5).

This example demonstrates that small changes in the model equations may sometimes cause unpredictably large changes in the results. Model validation is needed to detect such errors.

───── **Example 2** ─────

A Chemistry Problem[10]

This problem has been frequently used to test stiff ODE solver programs, and it is cited very often in both the chemical engineering[8] and numerical analysis[11,p.734] literature.

The equations of this example, as they appear in reference 11 are

$$\frac{dy_1}{dt} = -0.013\, y_1 - 1000\, y_1 y_3 \tag{6a}$$

$$\frac{dy_2}{dt} = -2500\, y_2 y_3 \tag{6b}$$

$$\frac{dy_3}{dt} = -0.013\, y_1 - 1000\, y_1 y_3 - 2500\, y_2 y_3 \tag{6c}$$

The initial conditions are $y_1(0)=1$, $y_2(0)=1$, and $y_3(0)=0$. These equations are usually integrated from $t_o = 0$ up to $t_f = 50$. Assuming that y_1, y_2, and y_3 represent concentration of different species, the students should check the physical feasibility of the solution.

The variation of y_3 in the requested time interval is shown as curve "A" in Figure 2. It can be seen that y_3 descends very rapidly from the initial values $y_3(0)=0$ to $y_3=-3.7 \times 10^{-6}$ and stays negative for the whole range of solution. Assuming that y_3 represents concentration (a very probable assumption given the form of the model equations), it cannot be negative.

The original reference by Gear[10] shows that there was a typographical error in Eq. (6c). The equal sign is missing and there is a minus sign in front of the 0.013 y_1 term.
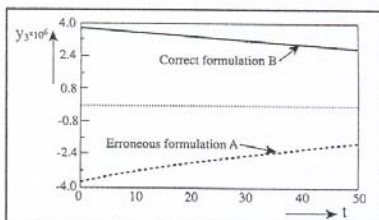
Figure 2. *Variation of y_3 in the chemistry problem in a large time scale*
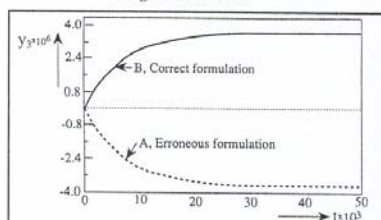

Figure 3. *Variation of y_3 in the chemistry problem in a short time scale.*

Apparently when the equation was copied by others, the equal sign was added and the minus sign was retained. This formulation of the problem gives a physically infeasible solution of a negative concentration of y_3. The general form of Eq. (6) indicates that it most probably represents reaction rates among three reacting species, so the 0.013 y_1 term in Eq. (6c) must definitely be positive.

The integration when the first minus is replaced by a plus in Eq. (6c) yields all positive values for y_3 as shown in Figure 2 (curve "B"). Figure 2 demonstrates an additional potential problem in interpreting the results. Since the initial change of y_3 is very fast, it seems from the figure that the initial value of y_3 is $y_3(0)=3.27 \times 10^{-6}$ (or -3.27×10^{-6}) instead of the correct value of $y_3(0)=0$. To see the exact details of the solution at initial t, the integration interval must be reduced considerably. Figure 3 shows the initial changes of y_3 when the integration interval is reduced by a factor of 10^{-3}.

This example demonstrates that error in the model often

TABLE 2
Multiple Solutions of the Chemical Equilibrium Problem

Variable	1	2	3
C_D	0.7053	0.0556	1.0702
C_X	0.1778	0.5972	-0.3225
C_Z	0.3740	1.0821	1.1304
C_A	0.4207	-0.3624	-0.7007
C_B	0.2429	-0.2348	0.8080
C_C	0.1536	-1.6237	-0.3782
C_Y	0.5518	1.6793	0.2623

results in physically infeasible solution, and that often the plot interval must be changed in order to obtain complete details of a solution.

Example 3

Chemical Equilibrium

The following system of algebraic equations describes equilibrium in a constant volume, gas-phase batch reactor for a complex system of reactions:

$$f_1(C_D, C_X, C_Z) = \frac{C_C C_D}{C_A C_B} - K_1 = 0$$

$$f_2(C_D, C_X, C_Z) = \frac{C_X C_Y}{C_C C_B} - K_2 = 0$$

$$f_3(C_D, C_X, C_Z) = \frac{C_Z}{C_A C_X} - K_3 = 0$$

$$C_A = C_{AO} - C_D - C_Z$$
$$C_B = C_{BO} - C_D - C_Y$$
$$C_C = C_D - C_Y$$
$$C_Y = C_X - C_Z \qquad (7)$$

where C_A, C_B, C_C, C_D, C_X, C_Y, and C_Z are concentrations of the various species, and C_{AO}, C_{BO}, K_1, K_2, and K_3 are constants.

The assignment is to solve the system for the following values of the constants:

$$C_{AO} = C_{BO} = 1.5$$
$$K_1 = 1.06$$
$$K_2 = 2.63$$
$$K_3 = 5$$

for three different sets of initial estimates

$$(C_D, C_X, C_Z) = 0, 1, 10$$

Most programs for solving nonlinear algebraic equations will not be able to solve this system (7) as it is written. The difficulty is caused by division by the unknowns in the first three equations. The problem can be made much less nonlinear and easier to solve by eliminating division by the unknowns. Indeed, f_1 can be multiplied by $C_A C_B$ to yield $C_C C_D$ - $K_1 C_A C_B = 0$. Similar transformations can be applied to f_2 and f_3. Using the modified set of equations POLYMATH converged to three different solutions (as shown in Table 2) from the three initial guesses.

Checking for physical feasibility reveals that only the first solution is acceptable. In solutions 2 and 3, some of the concentrations are negative, and thus these solutions cannot represent a valid physical situation.

Contrary to dynamic simulation, in solving steady-state models, the algorithm may converge to infeasible solutions, even when the model is correct and the initial estimate lies in the feasible region. If an infeasible solution is reached, a sensitivity analysis (by changing the initial guess) should be carried out in an attempt to locate a feasible solution. In this

case, convergence to infeasible solutions does not necessarily indicate an erroneous model.

Example 4

Equilibrium Conversion in an Isothermal Tubular Reactor

The following equations represent the conversion in a tubular reactor (X) as a function of the catalyst weight (w):

$$\frac{dX}{dw} = \frac{\dfrac{k_1 P_0 (1-X)}{1+X} - \dfrac{k_2 P_0^2 X^2}{(1+X)^2}}{F_{AO}\left[1 + 7\, P_0 \dfrac{(1-X)}{(1+X)}\right]} \tag{8}$$

where

$k_1 = 1.277 \times 10^9 \exp^{[-90000/(8.31\,T)]}$

$k_2 = 1.29 \times 10^{11} \exp^{[-135000/(8.31\,T)]}$

$F_{AO} = 20\, P_0 /(0.082 \times 450)$

P_0 = pressure at the inlet

T = temperature in the reactor

The assignment is to find the equilibrium conversion in the reactor for $P_0 = 10$ atm and $T = 313\,°K$.

To find the equilibrium conversion in the reactor, $dX/dw = f(X)$ is set to zero. Solving the resultant algebraic equation using the POLYMATH 3.0[12] program yields two solutions:

$X = 0.984$ where $f(X) = 0.114 \times 10^{-7}$

and

$X = 1.02$ where $f(X) = -0.7 \times 10^{-7}$

At both points the function value is very small, and thus both can represent legitimate solutions. But conversion of 1.02 is unacceptable because it is physically infeasible to obtain conversion higher than 1.

Carrying out sensitivity analysis, by changing the initial guess for the unknown X, causes the program to find different values for the first solution. A plot of $f(X)$ versus X (shown in Figure 4) reveals the reason for the inability of the program to locate the root precisely. Between $X = 0$ and $X = 1$ the function value is always below the 3×10^{-8} in absolute value. There are two changes of the function value sign around $X = 1$. One at the root (the precise value is $X = 0.999985$) and the other at $X = 1.029$, which is a point of discontinuity for the function. With such small function values throughout the entire interval of interest and the presence of point of discontinuity near the solution, most programs will have great difficulty in locating the precise root.

Once a solution is reached, the root must be verified. For verification, the values of the unknown must be introduced into the functions to yield values close to zero. In some of the nonlinear equation-solver programs, the user must explicitly request calculation and display of the function values
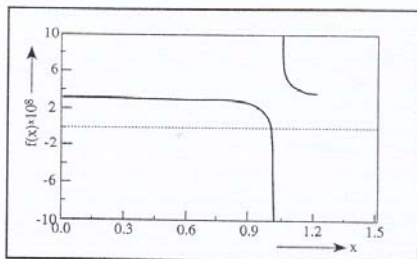
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Figure 4. Function shape for equilibrium conversion calculation in a tubular flow reactor.

at the solution. This is essential for avoiding acceptance of incorrect results, as may happen when the program uses minimization algorithms and occasionally converges to a local minimum. More strict verification of the root is possible by carrying out a sensitivity study to obtain changes of the sign of the function values in the vicinity of the solution.

Example 5

Aerobic Microbial Growth Problem[13]

The following equation represents the amount of substrate (S), cells (x), and concentration of oxygen (C_{O_2}) in an aerobic microbial growth system:

$$\frac{dx}{dt} = \mu x$$

$$\frac{dS}{dt} = -\frac{\mu x}{Y_{x/s}} - mx$$

$$\frac{dC_{O_2}}{dt} = K_{LA}\left(C_{O_2}^* - C_{O_2}\right) - \frac{\mu x}{Y_{x/O_2}} - \frac{m_{O_2}}{x} \tag{9}$$

where

$$\mu = \mu_{max} \frac{S}{K_S + S}$$

$\mu_{max}, K_S, Y_{x/s}, Y_{x/O_2}, m, K_{LA}, C_{O_2}^*, m_{O_2}$ = constants.

The assignment is to explore the dynamics of this system from $t = 0$ to $t = 10$ hrs using the constants and initial values shown in Table 3.

Figure 5 shows the variation of the biomass with time. It can be seen that the amount of biomass increases up to around $t = 0.65$ and from this point on the amount decreases (as indicated by the curve of the original model). Checking the physical feasibility for the other variables reveals that when x reaches its maximum, the substrate value is reduced to zero. It continues to decrease and obtains negative values. This is, of course, impossible. The reason for the negative amounts of material, in this case, is that the model presented in Eq. (9) is correct only if $S > 0$. In order to make the same model applicable for the $S = 0$, the differential equation dS/dt must be rewritten as

$$\frac{dS}{dt} = \begin{cases} -\dfrac{\mu x}{Y_{x/s}} - mx & \text{if } S > 0 \\[2mm] 0 & \text{otherwise} \end{cases} \qquad (10)$$

Using the revised model x remains constant after reaching its maximum, as shown in Figure 5. Thus the original model was used outside the region of its validity, and proper model validation procedure detects this problem.

If, during dynamic simulation, some of the variables become infeasible at a particular point, sensitivity analysis (by changing tolerances or parameters of the numerical solution algorithm) at the vicinity of this point can detect whether the source of the problem lies in the numerical solution algorithm or the model fails to represent correctly the physical situation at this point.

DISCUSSION AND CONCLUSIONS

We have shown five examples where computational results can be incorrect. The following reasons for incorrect or imprecise results were demonstrated: carelessly rounding numbers in the model equations; error in the sign in a model equation; multiple problem solutions; using a model outside the domain of its validity; numerical difficulties in finding the precise solution when working with very small numbers.

There can be many more reasons for obtaining incorrect results. Correlation of experimental data when the model equations are improperly linearized[14] or when experimental design for obtaining the data is not satisfactory[15] can be common sources of such errors. Low resolution in presenting the results can lead to misinterpretation of the results even if the solution is correct.[16]

In an era when hand calculations have been replaced by computation, it is more important than ever to consistently validate and verify the results. The examples provided in this paper demonstrate very clearly the necessity of model validation. The suggested procedures can serve as a basis for systematic approach for validating the results.

TABLE 3
Constants and Initial Values for the Microbial Growth Problem[13]

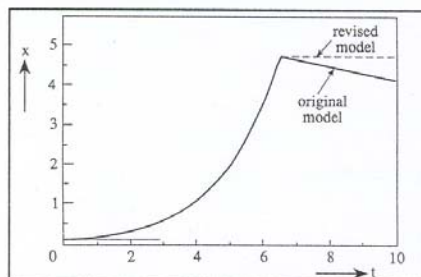| Constant	Value	Units
μ_{max}	0.6	hr^{-1}
K_s	0.05	gr/liter
$Y_{x/s}$	0.5	gr · cells/gr · glucose
Y_{x/O_2}	1	gr · cells/gr · O_2
m	0.08	gr · glucose/(gr · cells · hr)
K_{LA}	400	hr^{-1}
$C_{O_2}^*$	8	mgr/liter
m_{O_2}	0.1	gr · O_2/(gr · cells · hr)
x(t=0)	0.1	gr/liter
S(t=0)	10	gr/liter
C_{O_2} (t=0)	8	mgr/liter

Figure 5. Variation of the biomass in the microbial growth problem.

REFERENCES

1. Mah, R.S.H., and D.M. Himmelblau, "Role and Impact of Computers in Engineering Education," *Chem. Eng. Ed.*, 29(1), 46 (1995)
2. Davis, J.R., G.E. Blau, and G.V. Reklaitis, "Computers in Undergraduate Chemical Engineering Education," *Chem. Eng. Ed.*, 29(1), 46 (1995)
3. Himmelblau, D.M., "Mathematical Modeling," p 35 in Bisio, A., and R.L. Kabel, eds, *Scaleup of Chemical Processes*, John Wiley, New York, NY (1985)
4. Finger, G.S., and T.H. Naylor, *Mang. Sci.*, 14, 92 (1967)
5. Riggs, J.B., "A Systematic Approach to Modeling," *Chem. Eng. Ed.*, 22, 26 (1988)
6. Luss, D., and N.R. Amundson, "Stability of Batch Catalytic Fluidized Beds," *AIChE J.*, 14(2), 211 (1968)
7. Aiken, R.C., and L. Lapidus, "An Effective Numerical Integration Method for Typical Stiff Systems," *AIChE J.*, 20(2), 368 (1974)
8. Enright, W.H., and T.E. Hull, "Comparing Numerical Methods for the Solution of Stiff Systems of ODEs Arising in Chemistry," p 45 in Lapidus, L., and W.E. Schiesser, eds, *Numerical Methods for Differential Systems*, Academic Press, Inc., New York, NY (1976)
9. Michelsen, M.L., "An Efficient General Purpose Method for the Integration of Stiff Ordinary Differential Equations," *AIChE J.*, 22(3), 594 (1976)
10. Gear, C.W., "The Automatic Integration of Stiff Ordinary Differential Equations," *Proc. of the IP68 Conf.*, North-Holland, Amsterdam (1969)
11. Press, W.H., S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes*, 2nd ed., Cambridge Univ. Press, Cambridge (1992)
12. Shacham, M., and M.B. Cutlip, *POLYMATH 3.0 User's Manual*, CACHE Corporation, Austin, TX (1993)
13. Bajpai, R., personal communication (1995)
14. Shacham, M., J. Wisniak, and N. Brauner, "Error Analysis of Linearization Methods in Regression of Data for the Van Laar and Margules Equations," *Ind. Eng. Chem. Res.*, 32, 2820 (1993)
15. Shacham, M., and N. Brauner, "Correlation and Overcorrelation of Heterogeneous Reaction Rate Data," *Chem. Eng. Ed.*, 29(1), 22 (1995)
16. Shacham, M., N. Brauner, and M. Pozin, "Pitfalls in Using General Purpose Software for Interactive Solution of Ordinary Differential Equations," presented at the ESCAPE5 Conference, Bled, Slovenia, June 11-14 (1995) ❏