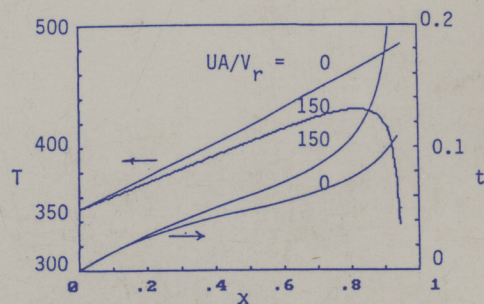
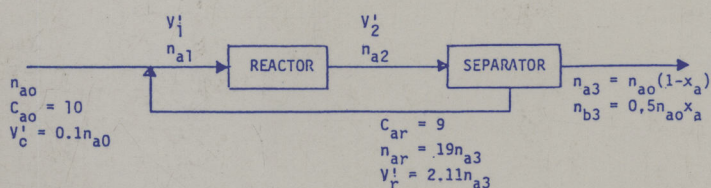
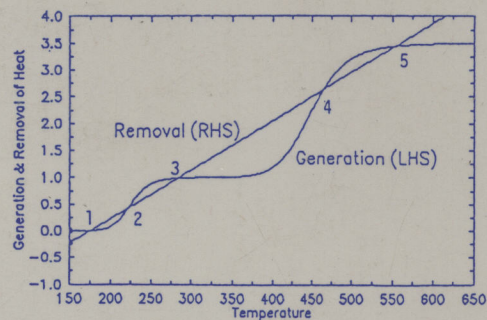
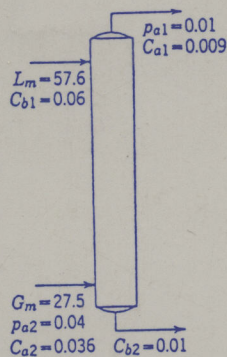
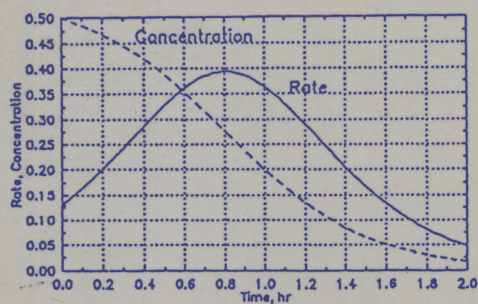
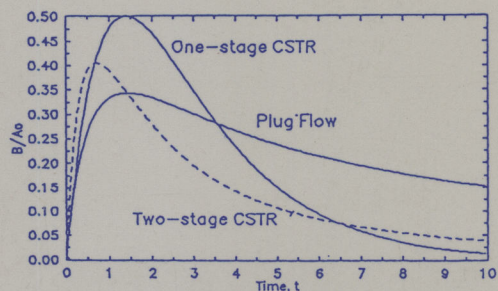


CHEMICAL REACTION ENGINEERING HANDBOOK OF SOLVED PROBLEMS

STANLEY M. WALAS



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Chemical Reaction Engineering Handbook of Solved Problems

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University of Kansas, Lawrence



Gordon and Breach Publishers

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PREFACE

This book is a collection of solved problems in elementary chemical reaction kinetics from an engineer's point of view. Brief statements of definitions and theory begin each chapter, but detailed derivations of major formulas largely are left as problems to be solved. Some of the problems are original to the extent that "originality" is possible in an area that has been worked over for so many years. Those taken from the literature and textbooks often are modified and provided with solutions when they are not in the original, which is usually the case. The List of Sources of Some Problems may be consulted for additional problems, although solutions usually are not provided in these references. Standard textbooks also should be consulted for systematic parallel or fuller treatment of some of the theory covered by this collection.

For the most part, the problems are quite short. The object has been to present a large variety of problems and exercises, including some replication for purposes of drill. Accordingly, comprehensive design-type problems largely have been avoided—those requiring detailed knowledge and data of other areas of engineering such as mass transfer or fluid dynamics or economics. The topics included are identified by chapter headings and subheadings. Briefly, they cover rate equations, analysis of rate data, sizes and performance of ideal reactors, residence time distributions and non-ideal models, solid catalyzed reactions, behavior of porous catalysts, and reactions involving multiple phases.

Solutions are presented in the form of equations, tables, and graphs—most often the last. Serious numerical results generally have to be obtained with computers or powerful calculators. The introductory chapter describes the numerical procedures that are required. Inexpensive software has been used here for integration, differentiation, nonlinear equations, simultaneous equations, systems of differential equations, data regression, curve fitting, and graphing.

Students, other beginners in chemical engineering kinetics, and possibly experienced engineers who may wish to review their rusty knowledge should be able to profit from the opportunities of "learning by doing" provided by this collection.

Reactors are of course the basic equipment in any chemical plant. The large variety of substances that have been used in the research cited in the problems emphasize this point. Also cited are the many different kinds of equipment, analytical techniques, and methods of data analysis that have been used. The Indexes of Substances and Subjects are the keys to this information.

Inspiration for the material in this book was provided by several generations of students; I hope that the current generation may find it of value. The word processor ChiWriter of Horstmann Software, Inc. was used. I appreciate the interest shown by Dr. Reza Shams and Professor Bala Subramaniam during the often tedious course of preparation of the manuscript. My parents Stanislaus and Apolonia and my wife Suzy Belle were with me in spirit.

SOURCES OF SOME PROBLEMS

- Aris, R, *Introduction to the Analysis of Chemical Reactors*, Prentice-Hall, Englewood Cliffs, NJ, 1965.
- Aris, R, *Elementary Chemical Reactor Analysis*, Prentice-Hall, Englewood Cliffs, NJ, 1969.
- Bares, J, *Collection of Problems in Physical Chemistry*, Addison-Wesley, Reading, MA, 1962.
- Batalin, GI, *Collection of Examples and Problems in Physical Chemistry*, Kiev University Publishers, Russia, 1960.
- Butt, JB, *Reaction Kinetics and Reactor Design*, Prentice-Hall, Englewood Cliffs, NJ, 1980.
- Capellos, C, BHJ Bielski, *Kinetic Systems: Mathematical Description of Chemical Kinetics in Solution*, Wiley, New York, NY, 1972.
- Carberry, JJ, *Chemical and Catalytic Reaction Engineering*, McGraw Hill, New York, NY, 1976.
- Chen, NH, *Process Reactor Design*, Allyn & Bacon, 1983.
- Cooper, AR, GV Jeffreys, *Chemical Kinetics and Reactor Design*, Prentice-Hall, Englewood Cliffs, NJ, 1971.
- Espenson, JH, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, NY, 1981.
- Fogler, HS, *Elements of Chemical Reaction Engineering*, Prentice-Hall, Englewood Cliffs, NJ, 1992.
- Froment, GF, KB Bischoff, *Chemical Reactor Analysis and Design*, Wiley, New York, NY, 1990.
- Fromherz, H, *Physico Chemical Calculations in Science and Industry*, Butterworths, Newton, MA, 1964.
- Frost, AA, RG Pearson, *Kinetics and Mechanism*, Wiley, New York, NY, 1961.
- Griffiths, PJF, JDR Thomas, *Calculations in Advanced Physical Chemistry*, Edward Arnold, London, UK, 1983.
- Guggenheim, EA, JE Prue, *Physicochemical Calculations*, Interscience, New York, NY, 1955.
- Hill, CG, *An Introduction to Chemical Engineering Kinetics and Reactor Design*, Wiley, New York, NY, 1977.
- Holland, CD, RG Anthony, *Fundamentals of Chemical Reaction Engineering*, Prentice-Hall, Englewood Cliffs, NJ, 1989.
- Levenspiel, O, *Chemical Reaction Engineering*, Wiley, New York, NY, 1972.
- Pannetier, G, P Souchay, *Chemical Kinetics*, Elsevier, New York, NY, 1967.
- Pratt, GL, *Gas Kinetics*, Wiley, New York, NY, 1969.
- Sillen, LG, PW Lange, CO Gabrielson, *Problems in Physical Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1952.
- Smith, JM, *Chemical Engineering Kinetics*, McGraw-Hill, New York, NY, 1981.
- Swinbourne, ES, *Analysis of Kinetic Data*, Nelson, Chicago, IL, 1971.
- Walas, SM, *Reaction Kinetics for Chemical Engineers*, McGraw-Hill, New York, NY, 1959; Butterworths, Newton, MA, reprint 1989.
- Walas, SM, *Modeling with Differential Equations in Chemical Engineering*, Butterworth-Heinemann, Newton, MA, 1991.
- Westerterp, KR, WPM van Swaaij, AACM Beenackers, *Chemical Reactor Design and Operation*, Wiley, New York, NY, 1984.
- Wolfenden, JH, RE Richards, EE Richards, *Numerical Problems in Advanced Physical Chemistry*, Oxford, New York, NY, 1964.

SYMBOLS

A, B, C, ...	names of substances, or their concentrations
A \cdot	free radical, as CH $_3\cdot$
C $_a$	concentration of substance A
C o	initial mean concentration in vessel, p. 506, 508
C $_p$	heat capacity
CSTR	Continuous Stirred Tank Reactor
D, D $_o$, D $_x$	dispersion coefficient, p. 500, 617, 629
D $_{off}$	effective diffusivity, p. 721
D $_k$	Knudsen diffusivity, p. 721
E(t)	residence time distribution, p. 507, 508
E (t)	normalized residence time distribution, p. 508
f $_a$	= C $_a$ /C $_{a0}$ or n $_a$ /n $_{a0}$, fraction of A remaining unconverted
F(t)	Age Function of tracer, p. 506, 508
ΔG	Gibbs energy change, p. 249
Ha	Hatta number, p. 828, 829
ΔH_r	heat of reaction
K, K $_c$, K $_y$, K $_p$	chemical equilibrium constant, p. 248
k, k $_c$, k $_p$	specific rate of reaction, p. 35, 103
L	length of path in reactor
n	parameter of Erlang or Gamma distribution, or number of stages in a CSTR battery, p. 497
n $_a$	number of mols of A present
n' $_a$	number of mols flowing per unit time, the prime (') may be omitted when context is clear
n $_t$	total number of mols

o	subscript designating initial or inlet conditions, as in C_{o0} , n_{o0} , V'_{o0} , ...
p_a	partial pressure of substance A
Pe	Peclet number for dispersion, p. 617
PFR	Plug Flow Reactor
Q	heat transfer rate
r	radial position
r_a	rate of reaction of A per unit volume, p. 34
R	radius of cylindrical vessel
Re	Reynolds number, p. 627, 717
Sc	Schmidt number, p. 627, 717
t	time
\bar{t}	mean residence time, p. 506, 508
t_r	= t/\bar{t} , reduced time
TFR	Tubular Flow Reactor
u	linear velocity
$u(t)$	unit step input, p. 492
V	volume of reactor contents
V'	volumetric flow rate
V_r	volume of reactor
x	axial position in a reactor
x_a	= $1 - f_a = 1 - C_a/C_{a0}$ or $1 - n_a/n_{a0}$, fraction of A converted
z	= x/L , normalized axial position
β	= r/R , normalized radial position, p. 410
$\gamma^3(t)$	skewness of distribution, p. 507, 508
$\delta(t)$	unit impulse input, Dirac function, p. 492
ε	fraction void space in a packed bed
ϑ	= t/\bar{t} , reduced time
η	effectiveness of porous catalyst, p. 724
$\Lambda(t)$	intensity function, p. 492, 508
μ	viscosity

ν	= μ/ρ , kinematic viscosity
π	total pressure
ρ	density
ρ	= r/R , normalized radial position in a pore, p. 723
$\sigma^2(t)$	variance, p. 507, 508
$\sigma^2(\bar{t}_i)$	normalized variance, p. 507, 508
τ	= t/\bar{t} , reduced time
τ	tortuosity, p. 722
ϕ	Thiele modulus, p. 723
ϕ_m	modified Thiele modulus, p. 731

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CHAPTER 1
MATHEMATICAL AND NUMERICAL METHODS

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The problems of this collection require numerical or graphical or sometimes analytical methods of solution. There is a large number of books and software on these topics. An outline with examples of these methods is the aim of this chapter. It is expected that the student will have access to some equivalents of the software used here for the solved problems and listed subsequently. Some of the work can be done with a programmable calculator, but not as easily as on a PC.

1.1. SOFTWARE

Of the following list, the first six items are the principal ones used here. All but TableCurve are currently available at reduced prices to students, but most of the required curvefitting also can be done with POLYMATH or AXUM. The last three items do analytical as well as numerical work.

1. POLYMATH. AIChE Cache Corp, P O Box 7939, Austin TX 78713-7939. Polynomial and cubic spline curvefitting, multiple linear regression, simultaneous ODEs, simultaneous linear and nonlinear algebraic equations, matrix manipulations, integration and differentiation of tabular data by way of curve fit of the data.

2. CONSTANTINIDES, Applied Numerical Methods with Personal Computers, McGraw-Hill, 1987. Nonlinear regression, partial differential equations, matrix manipulations, and a more flexible program for simultaneous ODEs.

3. CHAPRA & CANALE, Numerical Methods for Engineers, McGraw-Hill, 1988. Explains the methods but the diskette is limited. It does have the trapezoidal

rule for data in tabular or equation form.

4. SEQS simultaneous equation solver. CET, PO Box 2029, Norman OK 73070. Twenty simultaneous equations can be solved. The program seems to be superior to the one in POLYMATH.

5. AXUM. Trimetrix Inc, 444 NE Ravenna Blvd, Seattle WA 98115. High quality graphics and data analysis, including nonlinear regression.

6. TableCurve. Jandel Scientific, 65 Koch Road, Corte Madera CA 94925. Automatically fits 3000 different xy relations with statistical criteria.

7. MathCad Numerical Supplement. MathSoft 201 Broadway, Cambridge MASS 02139

8. Maple V. Brooks/Cole Publishing Company, Pacific Grove CA 93950.

9. Mathematica. Wolfram Research, 100 Trade Center Drive, Champaign ILLINOIS 61820-9910.

1.2. PLOTTING AND CURVE FITTING

Graphical representation and corresponding equations of tabular data are of value for interpolation, for revealing behavior patterns, and other purposes. The most complete software for this purpose is TableCurve. More limited but adequate for the present book are POLYMATH and MathCad. All spreadsheet software, for instance QuattroPro, can make plots of all kinds. In this book the most used software for making plots of tabular data and equations is AXUM which is also capable of fitting polynomials and nonlinear equations to tabular data. All of these commercial packages have tutorials and user friendly instructions.

1.3. REGRESSION OF TABULAR DATA

Regression is a process of representing tabular data, say (C,t), in equation form. The purpose may be

..For interpolation of intermediate values of C or t

..To obtain an equation, $C = f(t)$, that can be handled readily in a computer program

..To facilitate repeated differentiation or integration of the data.

The form of the equation is specified in advance, and the best corresponding values of any constants are found by least squares. The goodness of fit of several assumed equations are compared by statistical criteria such as the correlation coefficient or the F-test. When the number of sets of data equals the number of unknown constants in the equation, the constants are found by simultaneous solution. Otherwise a least squares regression is used.

Linearity refers to the unknown constants. The following are linear in this sense,

$y = a+bx+cx^2$ and $\ln y = a+b \ln x + c/x^2$
but not

$y = a + \frac{b}{x+c}$ and $y = \exp(a+\frac{b}{x}) x^c$

although the last can be linearized as

$\ln y = a + \frac{b}{x} + c \ln x$

There are four main classes of data regression.

1. Polynomial, $y = a_0 + a_1x + a_2x^2 + \dots$. Linear regression is a special case.

2. Multilinear, $y = a_0 + a_1x_1 + a_2x_2 + \dots$, where x_1, x_2, \dots are independent variables or functions.

3. Nonlinear, say of two variables, x and y,

$$y_i = f(x_i; a_0, a_1, a_2, \dots)$$

and the derivatives

$$\frac{\partial \Sigma}{\partial a_0} = \frac{\partial \Sigma}{\partial a_1} = \frac{\partial \Sigma}{\partial a_2} = \dots = 0$$

of the least squares condition,

$$\Sigma [y_i - f(x_i; a_0, a_1, a_2, \dots)]^2 \Rightarrow \text{Minimum}$$

are not linear in the unknown constants a_i .

4. Periodic data, using the Fast Fourier Transform.

These topics are explained in specialist books and briefly by CHAPRA & CANALE. Polynomial and multilinear regression programs are in POLYMATH and AXUM, nonlinear in CONSTANTINIDES and AXUM. No periodic data are regressed in the present collection.

Examples: Polynomial regression is applied in problem P1.03.02. Several examples of POLYMATH multilinear regression are in sections P3.06, P3.08 and P3.10. A non-linear regression is worked out in P1.02.07.

1.4. ROOTS OF NUMERICAL EQUATIONS

Methods for finding roots of numerical nonlinear equations first involve making estimates and subsequently improving them by some systematic procedure, ideal problems for implementation on computers. Many scientific calculators also have built-in capability for finding roots of single equations, for instance the HP-15C or HP-32SII.

1.4.1 SINGLE EQUATIONS

The Newton-Raphson method is based on the truncated Taylor expansion.

If x_0 is an estimate for $f(x) = 0$, an improved value is

$$x = x_0 - kf(x_0)/f'(x_0)$$

where $f'(x) = df/dx$ and k is a positive fraction that is selected arbitrarily to speed convergence; $k = 1$ often is acceptable. When the derivative is awkward to find analytically, a finite difference equivalent can be used, for instance,

$$f'(x) = \frac{f(1.0001x) - f(x)}{0.0001x}$$

Then,

$$x = x_0 - k \frac{0.0001x_0 f(x_0)}{f(1.0001x_0) - f(x_0)}$$

The factor 1.0001 is arbitrary and can be changed to improve convergence or accuracy.

Wegstein method. This does not require a derivative and usually converges more rapidly than the Newton-Raphson. The equation is put in the form

$$x = f(x)$$

When x_0 is the estimated value of the root and $x_1 = f(x_0)$, an improved value is

$$x = \frac{x_0 f(x_1) - f(x_0)^2}{x_0 + f(x_1) - 2f(x_0)} = \frac{x_0 f(x_1) - x_1^2}{x_0 + f(x_1) - 2x_1}$$

The process is repeated with the improved estimate as a start.

Polynomials, $a_0 + a_1x + a_2x^2 + a_3x^3 + \dots = 0$. Procedures for finding all real and complex roots are on the diskettes of CONSTANTINIDES and Al-Khafaji & Tooley (Computerized Numerical Analysis, 1986). For instance the roots of

$$x^6 - 3x^5 - 4x^4 - 9x^3 + 10x^2 + 2x + 3 = 0$$

are

$$x = -0.1438 \pm 0.1610j, -1.000 \pm 1.414j, 4.288, 1.000$$

1.4.2. SIMULTANEOUS LINEAR EQUATIONS

These are solved by matrix manipulations. Programs are in POLYMATH, CONSTANTINIDES AND CHAPRA & CANALE. When the number of equations is not large, a manual procedure can be used to eliminate one variable at a time by reduction of the leading coefficients to unity and appropriate additions and subtractions of the equations.

1.4.3. SIMULTANEOUS NONLINEAR EQUATIONS

The Newton-Raphson method for multiple equations also starts with truncated Taylor expansions. For the system

$$f(x,y,z) = 0, g(x,y,z) = 0, h(x,y,z) = 0$$

the corrections to initial estimates x_0, y_0, z_0 are a, b and c found from the linear system

$$f_0 + af_x + bf_y + cf_z = 0$$

$$g_0 + ag_x + bg_y + cg_z = 0$$

$$h_0 + ah_x + bh_y + ch_z = 0$$

where the functions and all the derivatives, for instance $f_x = \partial f/\partial x$, are evaluated at (x_0, y_0, z_0) . Programs are on the diskettes of POLYMATH and SEQS. The speed of convergence and even the possibility of convergence depend on how close the estimates are to the correct values. It is of course possible that there may not be a solution in the range of interest, or there may be several solutions.

1.5. INTEGRATION & DIFFERENTIATION

Only a comparatively few forms of integrals are encountered in reaction kinetics. Some of the more complex ones are reducible with partial fractions. Table 1.1 of indefinite integrals and partial fractions supplies most needs.

When integrating between numerical limits it may be more convenient to proceed directly with a numerical integration rather than through an analytical integration, particularly when the coefficients and integration limits are long numbers, for example, the integral

$$\int_{1.27}^{10.93} \frac{x}{2.1x^2 - 3.78x + 5.86} dx = 1.2811, 50 \text{ trapezoidal steps}$$

$$1.2815, 200 \text{ trapezoidal steps}$$

by CHAPRA & CANALE which takes a very simple input. Such a result may well be more reliable than the laborious evaluation of the analytical integral by way of item 11 of Table 1.1.

Softwares for numerical integration of equations include the calculator HP-32SII, POLYMATH, CONSTANTINIDES AND CHAPRA & CANALE. The last of these also can handle tabular data with variable spacing. POLYMATH fits a polynomial to the tabular data and then integrates. A comparison is made in problem P1.03.03 of the integration of an equation by the trapezoidal and Runge-Kutta rules. One hundred intervals with the trapezoidal rule takes little time and the result is usually accurate enough, so it is often convenient to standardize on this number.

For manual integration of tabular data, the trapezoidal or Simpson's rules usually are adequate. Between two points the trapezoidal rule is

$$\int_{x_1}^{x_2} y dx = 0.5(x_2 - x_1)(y_1 + y_2)$$

and between n points spaced equally with $\Delta x = x_n - x_{n-1}$ as interval,

$$\int_{x_0}^{x_n} y dx = \Delta x \left(\frac{y_0 + y_n}{2} + y_1 + y_2 + \dots + y_{n-1} \right)$$

Simpson's rule for three equally spaced points is

$$\int_{x_0}^{x_2} y dx = \frac{x_1 - x_0}{3} (y_0 + 4y_1 + y_2).$$

Differentiation. The main application of numerical differentiation in this book is to find a rate, dC/dt , from tabular data (C, t). In view of the availability of computer routines for fitting of polynomials and other equations to tabular data, this is the way to go, differentiating the curve fit equation analytically. POLYMATH can provide direct numerical values of derivatives and integrals from the curvefit result.

Numerical differentiation may be quite sensitive to the correlating equation. In problem P1.03.01, the results with four different curvefits do not agree well although the curvefits themselves are statistically satisfactory. In problem P1.0302, however, the agreement between the higher polynomial fits is more nearly acceptable.

1.6. ORDINARY DIFFERENTIAL EQUATIONS

Differential equations arise in reaction kinetics through application of two main fundamental rate laws, which are

1. The rate of reaction is proportional to the concentrations of the participants. Law of mass action.

2. The rate of transfer of mass (or heat) is proportional to the concentration gradient. Fick's law (or Newton-Fourier law).

1.6.1. FORMULATION

As a basis, a differential element of volume, $dV_r = dx dy dz$, or time, dt , is identified. In cylindrical geometry, the element of volume may be a thin disk, Adz , if changes occur only in an axial direction, or a ring $2\pi r dr dz$, if changes occur both radially and axially.

To this element of space the conservation law is applied in the form

$$\text{Inputs} + \text{Sources} = \text{Outputs} + \text{Sinks} + \text{Accumulations}$$

where each of these terms may be a quantity or a rate. Inputs and Outputs are accomplished by crossing the boundary of the reference volume. In case of mass transfer this occurs by bulk flow and diffusion. Sources and Sinks are accretions and depletions of a species without crossing the boundaries. In a mass and energy balance, sinks are the rate of reaction, $r dV_r$, or a rate of enthalpy change, $-\Delta H_r \rho dC$. Accumulation is the time derivative of the content of the species within the reference volume, for example, $(\partial C / \partial t) dV_r$ or $C_p (\partial T / \partial t) \rho dV_r$.

Conversion of the differential balance to a differential equation follows after division throughout by the differentials of space and time. Boundary and initial conditions are specified to complete the physical description of the problem. With ordinary differential equations the number of such conditions is the same as the order of the equation. With partial differential equations, the safest rule to follow is that the problem be completely defined in a physical sense. For example, the condition of every entering and/or leaving stream must be defined, the initial state of the vessel must be known (or a final state if the initial is to be found), symmetry conditions (such as radial symmetry) must be recognized if they exist in the particular problem, and conditions at the boundary such as rate of heat transfer or rate of reaction or rate of diffusion must be formulated

mathematically.

A detailed application of the conservation principle to the derivation of a second order equation is in problem P5.08.01.

1.6.2. INTEGRATION

Differential equations of the first order arise with application of the law of mass action under either steady or unsteady conditions, and second order with Fick's or Newton-Fourier laws. A particular problem may be represented by one equation or several that must be solved simultaneously.

Solutions of the commonest first order equations are listed in Table 1.2. Variables separable and first order linear are most often encountered. Exercises dealing with first order equations are in problem P1.05.05.

Sometimes an equation out of this classification can be altered to fit by change of variable. The equations with separable variables are solved with a table of integrals or by numerical means. Higher order linear equations with constant coefficients are solvable with the aid of Laplace Transforms. Some complex equations may be solvable by series expansions or in terms of higher functions, for instance the Bessel equation encountered in problem P7.02.07, or the equations of problem P2.02.17. In most cases a numerical solution is possible.

1.6.3. THE SECOND ORDER LINEAR ODE

Some problems with diffusion or dispersion give rise to the second order linear equation with constant coefficients,

$$\frac{d^2y}{dt^2} + 2k\omega \frac{dy}{dt} + \omega^2 y = f(t)$$

When $f(t) = 0$, the equation is called homogeneous. The general solution is the sum of the solution of the homogeneous equation and a complementary function which can be found by several means. The form of the homogeneous solution

depends on the value of the discriminant, $D = k^2 - 1$, as tabulated.

<u>Discriminant</u>	<u>Solution</u>
Positive	$y = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t)$
Zero	$y = (C_1 + C_2 t) \exp(-k\omega t)$
Negative	$y = \exp(-k\omega t) [C_1 \cos(\omega t \sqrt{1-k^2}) + C_2 \sin(\omega t \sqrt{1-k^2})]$
	$y = C \exp(-k\omega t) \cos(\omega t \sqrt{1-k^2} - \phi)$
	$y = C \exp(-k\omega t) \sin(\omega t \sqrt{1-k^2} + \phi)$

where $\lambda_1, \lambda_2 = \omega(-k \mp \sqrt{D})$, $C = \sqrt{C_1^2 + C_2^2}$, $\phi = \arctan(C_2/C_1)$

The complete solution of the non-homogeneous equation can be found directly in some cases by Laplace Transform, as the problems of section P1.04 show.

Several examples of second order equations are in problem section P5.08

1.6.4. LAPLACE TRANSFORM METHOD

The Laplace Transform of a function $f(t)$ is defined as

$$L\{f(t)\} = f(s) = \bar{f} = \int_0^{\infty} f(t) \exp(-st) dt$$

Several notations are in use, as indicated. Tables 1.3 and 1.4 summarize various operations and provide some pairs of functions and their transforms.