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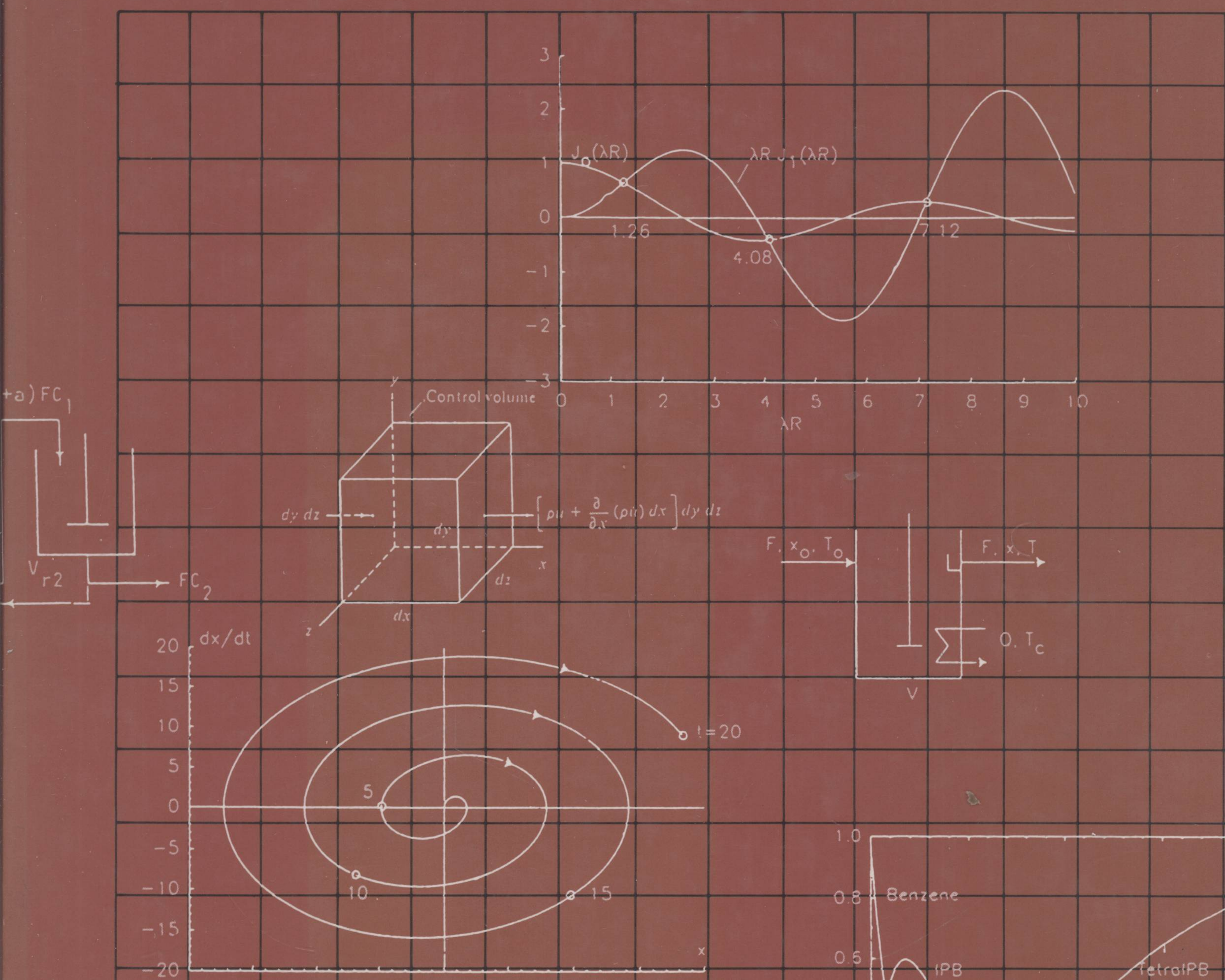
Modeling with Differential Equations in Chemical Engineering

Stanley M. Walas



Modeling with Differential Equations in Chemical Engineering

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To the memory of my parents,
Stanislaus and Apolonia,
and to my wife, Suzy Belle

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Preface

Two kinds of processes occur in the design and operation of chemical engineering equipment: (a) equilibrium processes, those in which the properties and conditions do not change with time, of which a prominent instance is the equilibrium stage of separating equipment; and (b) dynamic or rate processes, in which properties and conditions may change with time, or in which any property or condition is affected by variations in other properties or conditions. This book deals with major rate processes of interest to chemical engineers, mainly thermodynamics, mass transfer, heat transfer, fluid flow, chemical reactions, and automatic control. Full development of these topics, of course, is neither possible nor desirable here, and attention is restricted primarily to the differential equations that occur there.

Many physical laws are formulated as rate processes, from Newton's second law of motion and the law of mass action on. Mathematically, rates are represented by derivatives. Mathematical relations between derivatives and other functions constitute differential equations. Such equations are solved by eliminating derivatives from them.

To start, this books tells how to solve the main types of differential equations that occur in practice. Emphasis is placed early on numerical and approximate methods of solution, because the bulk of nontrivial problems have to be solved that way. To make way for the many desirable topics, the theoretical basis has had to be skimped, and preference has been given to detailed applications of methods of solution. For supplementary material on theoretical background and even for additional exercises, the reader is advised to consult conventional textbooks. The problems for the reader include some purely mathematical exercises, but the main emphasis is on problems of an engineering nature. Space and time are always short. The engineer who tries to learn everything that is known about a topic nowadays will have no time to solve his or her own problems.

After the mathematics of differential equations has been presented, a chapter is devoted to the principles of the mathematical formulation of engineering processes. Then follows the distinctive part of this book, which consists of derivations and solutions of differential equations in some of the major disciplines of chemical engineering. Many of the topics are reinforced by mathematical or numerical examples as well as problems for the reader, mostly with answers.

Little mathematics beyond calculus is expected of the reader. Computer usage by the examples and problems is restricted to readily available user-friendly PC diskettes, and essentially no individual programming is employed. The book should be accessible to third- or fourth-year undergraduates and possibly accessible to graduate students. Also, it should be of interest to professional engineers who have forgotten some of their schoolwork and wish to review or possibly extend some of it.

Although the applications are important to chemical engineers, many of them also should interest other engineers. The purely mathematical aspect of the book likewise should have a wider appeal.

Throughout my long industrial and academic career, I have been concerned with applied mathematics. Now I have found time to assemble this material partly for my own satisfaction, but I would like it to be of interest and perhaps of value to students and other engineers. It has had to be prepared without immediate student participation and thus has missed that baptism by fire. Several reviewers made helpful suggestions on the manuscript. Many of the figures were computer drawn by Said Saim, H.W. Kroeger, Dr. C.S. McCool, and Dr. M.J. Michnik also assisted with computerization. Professor Alkis Constantinides of Rutgers University graciously supplied improvements of his valuable diskette on numerical methods. Appreciation is due particularly to Dr. Reza Shams for his computer expertise and to Dr. Riyaz Kharrat for his mathematical advice, as well as for their faithful monitoring of the progress of the book—when is it going to be finished?

Contents

List of Examples

1

DIFFERENTIAL EQUATIONS AND THEIR SOLUTIONS

Differential equations are relations between several variables and their mathematical derivatives, for example,

1. $\frac{dy}{dx} = x + 5$ *first-order ordinary*
2. $\frac{d^2y}{dx^2} + 3\frac{dy}{dx} + 2y = 0$ *second-order*
3. $xy' + y = 3$ *linear*
4. $y''' + 2(y'')^2 + y' = \cos x$ *first-degree nonlinear*
5. $(y'')^2 + (y')^3 + 3y = x^2$ *second-degree nonlinear*
6. $\frac{\partial z}{\partial x} = z + x\frac{\partial z}{\partial y}$ *first-order partial*
7. $\frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} = x^2 + y$ *second-order partial*

They may arise out of physical laws that are expressed in terms of rates or as relations between forces, masses, and accelerations. Geometric relations between slopes and curvatures also may lead to differential equations of importance in engineering. For illustration, a number of relatively simple equations are derived in Example 1.1.

The tasks addressed in this book are both the formulation and the solution of differential equations that simulate engineering problems. For practical reasons, a mathematical simulation is sought from which meaningful conclusions can be drawn yet one that is not so complex that numerical results cannot be drawn in the available time with the available equipment.

Example 1.1

Differential Equations Originating in Some Physical Problems

(a) Dibromsuccinic acid decomposes in hot water at a rate that is proportional to its concentration, that is, $-dC/dt = kC$.

(b) A tank of volume V contains brine of concentration C_0. Fresh water is pumped in at a rate F, and solution overflows at the same rate. The solution is well stirred, so the effluent concentration is the same as that in the tank. Therefore, $-V\,dC/dt = FC$, with $C = C_0$ when $t = 0$.

(c) The motion of an object sliding on a horizontal surface is retarded by friction that is proportional to the velocity, $F_f = k\,dx/dt$. A constant force F_0 is impressed. By Newton's second law, the force balance is

$$F_0 - k\frac{dx}{dt} = m\frac{d^2x}{dt^2}$$

(d) Water evaporates from the surface of a porous material at a rate dW/dt that is proportional to the difference between the saturation humidity H_s and existing humidity H of the air. The humidity is the weight of moisture per unit volume. The room has a volume V. The material balance is

$$H = H_0 + \frac{W_0 - W}{V}$$

Accordingly, the rate of drying is

$$-\frac{dW}{dt} = k(H_s - H) = k\left(H_s - H_0 - \frac{W_0 - W}{V}\right)$$

(e) The bottom of a tank is covered with a layer of solid salt that dissolves at a rate that is proportional to the difference $C_s - C$ between the saturation and existing concentrations. The tank is stirred, and fresh water is pumped into the tank as in part (b). The material balance is

$$V\frac{dC}{dt} = k(C_s - C) - FC$$

(f) A crystal of $K_2Cr_2O_7$ falls through a column of pure water. Its velocity is given by Stokes's law as $dx/dt = k_1R^2$, where R is its radius. The rate of solution is proportional to the velocity. Putting it all together,

$$-\frac{d(4\pi R^3/3)}{dt} = k_2\frac{dx}{dt} = k_1k_2R^2$$

(g) By Newton's law, a body cools in air at a rate proportional to the difference in temperature, $T - T_{air}$, but the proportionality factor in still air varies as the 0.25 power of the temperature difference. Thus the relation becomes

$$-\frac{dT}{dt} = k(T - T_{air})^{1.25}$$

(h) A reacting system has the stoichiometric form $2A \to B \to C$. Substance A changes into B at a rate that is proportional to the square of its concentration. The balances on substances A and B are as follows, where the first equation is solved and substituted into the second to make it directly integrable.

$$-\frac{dA}{dt} = k_1A^2, \qquad A = \frac{A_0}{1 + k_1A_0t}$$

$$\frac{dB}{dt} = k_1A^2 - k_2B = k_1\left(\frac{A_0}{1 + k_1A_0t}\right)^2 - k_2B$$

(i) At each point (x, y) of a curve, the slope of the tangent equals the product of the abscissa and ordinate, that is,

$$\frac{dy}{dx} = xy$$

which has the solution $y = Ce^{x^2/2}$.

(j) The family of circles of fixed radius r with centers on the x axis has the equation

$$(x - C)^2 + y^2 = r^2$$

where C is an arbitrary constant. Elimination of C by differentiation leads to the differential equation of this family of curves,

$$y^2\left(\frac{dy}{dx}\right)^2 + y^2 = r^2$$

1.1. CLASSIFICATION, DEFINITIONS, AND CONCEPTS

An *ordinary differential equation* (ODE) involves functions and derivatives of only two variables, one independent and one dependent. Three kinds of symbols are used to designate the derivatives, as in these forms of the same equation:

$$\frac{d^2y}{dx^2} + xy\frac{dy}{dx} + y^2 = f(x, y)$$

$$y'' + xyy' + y^2 = f(x, y)$$

$$D^2y + xyDy + y^2 = f(x, y)$$

A *partial differential equation* (PDE) involves partial derivatives of one or more dependent variables with respect to more than one independent variable and functions of some or all of the variables.

The *order* of a differential equation is the order of the highest derivative. The equation $d^3y/dx^3 + (dy/dx)^2 + xy = 0$ is of the third order.

A *linear differential equation* does not have powers or products of the dependent variables and their derivatives. The general linear ODE of the nth order is $\Sigma_n^0 f_n(x)\, d^ny/dx^n = 0$. All other ODEs are nonlinear.

The *degree* of an equation that can be written as a polynomial in the dependent variable and its derivatives is the highest exponent on the highest derivative. The equation $(d^2y/dx^2)^3 + f(x, y)(dy/dx)^4 + g(x, y) = 0$ is of the third degree. Just as algebraic equations of high degree have multiple roots, differential equations of high degree have multiple solutions.

The *solution* of an ODE of the nth order,

$$F\left(x, y, \frac{dy}{dx}, \ldots, \frac{d^ny}{dx^n}\right) = 0$$

has n arbitrary constants and can be written

$$f(x, y, C_1, \ldots, C_n) = 0$$

or explicitly as

$$y = f(x, C_1, \ldots, C_n)$$

In specific cases, the constants C_i can be evaluated by imposing n conditions on the dependent variable or its derivatives. Conditions are of two kinds, initial value or one-point conditions, and boundary value or multiple-point conditions.

In *initial value problems*, values of the dependent variable and $n - 1$ derivatives are specified at a point x_0. For example, the equation $d^2y/dx^2 + y = 0$ has the solution $y = C_1 \sin x + C_2 \cos x$. The constants C_1 and C_2 can be evaluated when y_0 and y_0' are specified at x_0, by solving the two equations

$$y_0 = C_1 \sin x_0 + C_2 \cos x_0 \quad \text{and} \quad y_0' = C_1 \cos x_0 - C_2 \sin x_0$$

In *boundary value problems*, the n values of the dependent variable or its derivatives are specified at more than one point. Such problems do not always have unique solutions and may, in fact, have no solution. Example 2.8 illustrates this point. In practical problems, care must be taken to make multiple-point conditions compatible with each other.

Uniqueness of Solutions. The solution of a differential equation $y' = f(x, y)$ is unique at a point (x_0, y_0) if the function is continuous and its derivative $\partial f/\partial y$ is bounded (Cauchy's existence theorem). Geometrically this means that only one integral curve passes through (x_0, y_0). The points of a region at which the uniqueness of a solution is violated are called *singular points*; at such points, zero, one, or multiple solutions may exist. Example 1.2 examines some cases.

Singular solutions are those that cannot be obtained by assigning particular values to the integration constants of a general solution. Usually they are associated with nonlinear differential equations. *Envelopes*, for instance, have every point coincident with a point of each member of a family of curves representing the general solution. Example 1.3 considers a number of such cases.

Example 1.2
Domain of Existence and Uniqueness of Solutions

(a) The equation $dy/dx = x(1 - y^2)^{1/2} = f(x, y)$ has the derivative $\partial f/\partial y = -xy/(1 - y^2)^{1/2}$, which is bounded by $|y| \le 1$. Moreover, the function f itself is continuous over $|y| \le 1$. Consequently, the differential equation has a unique solution in any strip $-1 < y < 1$.

(b) For the equation $dy/dx = f(x, y) = x^2 - y^2$, the valid domain is the entire xy plane, because f is continuous everywhere and the derivative $\partial f/\partial x = -2y$ is not bounded.

(c) For the equation $dy/dx = y/(y - x) = f(x, y)$, the derivative is $\partial f/\partial x = -x/(y - x)^2$. At $y = x$, the function f is not continuous, and its derivative is unbounded, so the solution of the differential equation is not necessarily unique at that location.

(d) Table 2.4 gives several examples of the behavior of integral curves in the vicinity of singular points.

(e) In Example 1.3(b), the domain of existence of the solution is between the lines $y = x$ and $y = -x$ on the xy plane.

(f) In Figures 1.1c and 1.1f, the domains of existence are limited to portions of the xy plane.

Example 1.3
Envelopes as Singular Solutions

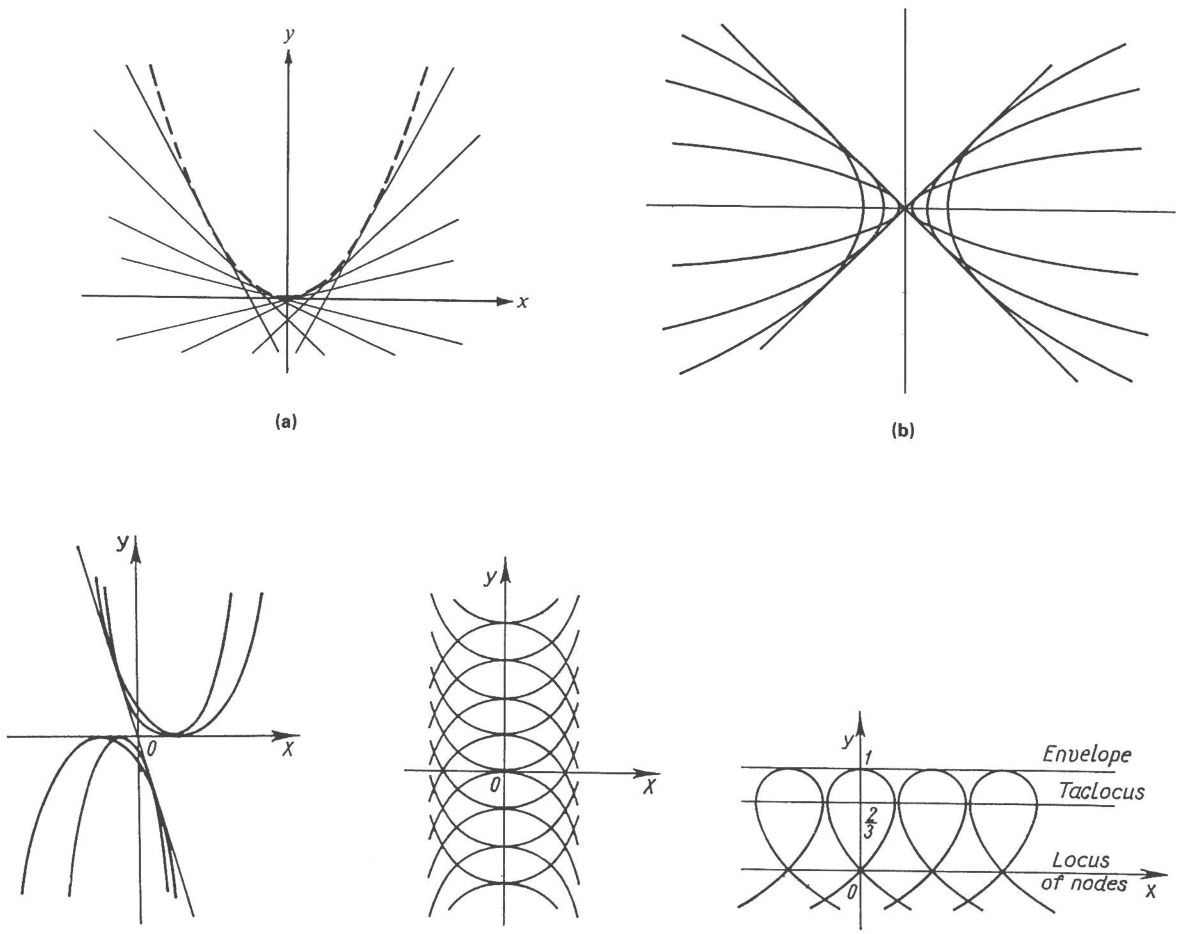
(a) The differential equation is $y = xy' - (y')^2/4$, and its solution is $y = Cx - C^2/4$, a family of straight lines. The envelope $y = x^2$ also is a solution of the differential equation but is not included in the general solution.

(b) The solution of a differential equation is $y^2 = 2Cx + C^2$, a family of parabolas. The derivative is $dy/dC = (x - C)/y = 0$. Eliminating C gives $y = x$ or $y = -x$, which are two straight lines, as the envelopes of the family of parabolas. Figure (b) represents this system.

(c) The differential equation is $2y(y' + 2) = x(y')^2$, whose general solution is $y = (C - x)^2/C$. The straight lines $y = 0$ and $y = -4x$ are the envelopes.

(d) The differential equation is $(y')^2 = 4x^2$, with general solution $y = x^2 + C$ and $y = -x^2 + C$, two families of parabolas. The straight line with equation $x = 0$ is the taclocus of the integral curves.

(e) For the differential equation $(y')^2(2 - 3y)^2 = 4(1 - y)$, the integral is $y^2(1 - y) = (x - C)^2$. The equation of the envelope is $y = 1$, that of the taclocus is $y = \frac{2}{3}$, and that of the locus of nodes is $y = 0$.



Geometrical Interpretation of a Differential Equation. The first-order differential equation represents a *direction field* on the xy plane. A solution is represented by a curve going through point (x_0, y_0) and following the direction field. This concept is illustrated in Figure 1.1a. Other parts of this figure show plots of solutions of several differential equations. Each curve corresponds to a particular value of an integration constant C. In parts (b), (c), and (e), every point in the plane has some curve passing through it; in part (d), only the region corresponding to the positive y axis is covered; and in part (f) the region covered with curves is a narrow strip.

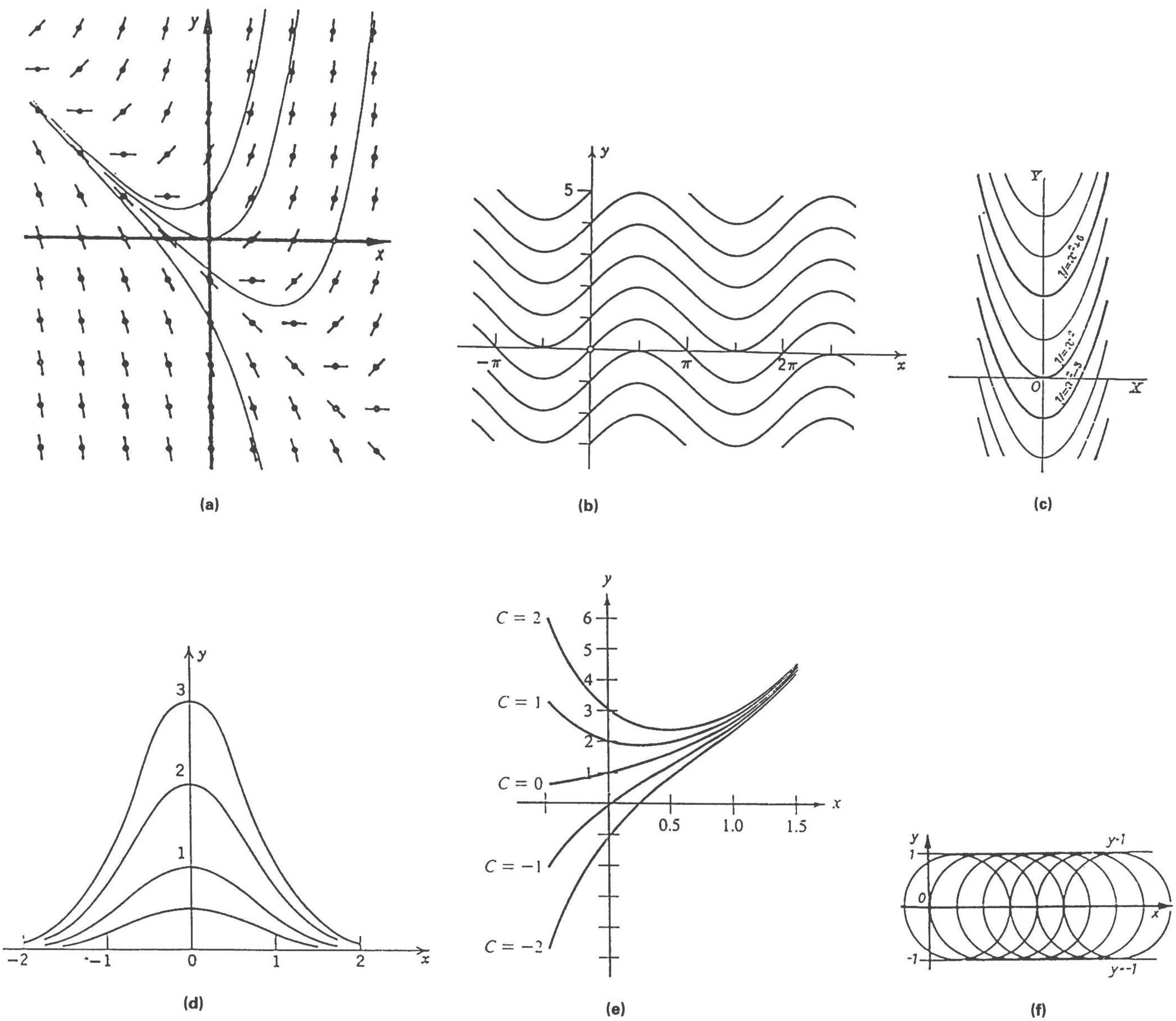


Figure 1.1. Direction fields and families of curves defined by differential equations. (a) Direction field and integral curves defined by $dy/dx = x + y$, with the integral $y = x - 1 + Ce^x$; a curve passes through every point of the plane. (b) Family of curves defined by $dy/dx = \cos x$, with integral $y = \sin x + C$; the whole plane is covered. (c) The equation $dy/dx = 2x$ has the integral $y = x^2 + C$; a curve through any point in the plane is determined by the value of the integration constant C. (d) A family of curves defined by $dy/dx + 2xy = 0$ with the integral $y = C\exp(-x^2)$; only the positive y plane is covered. (e) Family of curves defined by $dy/dx + 2y = 3e^x$, with integral $y = e^x + Ce^{-2x}$; the whole plane is covered. (f) Family of circles defined by $dy/dx = (a^2 - y^2)^{1/2}/y$, with integral $(x - C)^2 + y^2 = a^2$, occupying a band of width $2a = 2$.

1.2. METHOD OF ISOCLINES

An isocline is the locus of a function, $f(x, y, y' = c) = 0$, at a constant value of the derivative $y' = dy/dx$. The equation of the locus can be written $y = f(x, y'_{\text{fixed}})$. A field of closely spaced isoclines can be used in the construction of an integral curve of the equation. Start at a particular point (x_0, y_0), proceed in the direction corresponding to the isocline through that point to the neighboring isocline, change direction there, and so on. This is a feasible method of integration of a differential equation only if the isoclines can be constructed easily, such as the straight lines of Figure 1.2a or the circles of Figure 1.2b; the trigonometric isoclines of Figure 1.2c may be considered impractical.

Other graphical methods of drawing integral curves are described in the older literature—for example, by Willers (1948) and by