THE MATHEMATICS OF

PHYSICS AND CHEMISTRY

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PREFACE

The authors' aim has been to present, between the covers of a single book, those parts of mathematics which form the tools of the modern worker in theoretical physics and chemistry. They have endeavored to do this by steering a middle course between the mere recording of facts and formulas which is typical of handbook treatments, and the ponderous development which characterizes treatises in special fields. Therefore, as far as space permitted, all results have been embedded in the logical texture of proofs. Occasionally, when full demonstrations are lengthy or not particularly illuminating with respect to the subject at hand, they have been omitted in favor of references to the literature. Except for the first chapter, which is primarily a survey, proofs have always been given where omission would destroy the continuity of treatment.

Arbitrary selection of topics has been necessary for lack of space. This was based partly on the authors' opinions as to the relevance of various subjects, partly on the results of consultations with colleagues. The degree of difficulty of the treatment is such that a Senior majoring in physics or chemistry would be able to read most parts of the book with understanding.

While inclusion of large collections of routine problems did not seem conformable to the purpose of the book, the authors have felt that its usefulness might be augmented by two minor pedagogical devices: the insertion here and there of fully worked examples illustrative of the theory under discussion, and the dispersal, throughout the book, of special problems confirming, and in some cases supplementing, the ideas of the text. Answers to the problems are usually given.

The degree of rigor to which we have aspired is that customary in careful scientific demonstrations, not the lofty heights accessible to the pure mathematician. For this we make no apology; if the history of the exact sciences teaches anything it is that emphasis on extreme rigor often engenders sterility, and that the successful pioneer depends more on brilliant hunches than on the results of existence theorems. We trust, of course, that our effort to avoid rigor mortis has not brought us dangerously close to the opposite extreme of sloppy reasoning.

A careful attempt has been made to insure continuity of presentation within each chapter, and as far as possible throughout the book. The diversity of the subjects has made it necessary to refer occasionally to chapters ahead. Whenever this occurs it is done reluctantly and in order to avoid repetition.

As to form, considerations of literacy have often been given secondary rank in favor of conciseness and brevity, and no great attempt has been made to disguise individual authorship by artificially uniformising the style.

The authors have used the material of several of the chapters in a number of special courses and have found its collection into a single volume convenient. To venture a few specific suggestions, the book, if it were judged favorably by mathematicians, would serve as a foundation for courses in applied mathematics on the senior and first year graduate level. A thorough introductory course in quantum mechanics could be based on chapter 2, parts of 3, 8 and 10, and chapter 11. Chapters 1, 10 and parts of 11 may be used in a short course which reviews thermodynamics and then treats statistical mechanics. Reading of chapters 4, 9, and 15 would prepare for an understanding of special treatments dealing with polyatomic molecules, and the liquid and solid state. Since ability to handle numerical computations is very important in all branches of physics and chemistry, a chapter designed to familiarize the reader with all tools likely to be needed in such work has been included.

The index has been made sufficiently complete so that the book can serve as a ready reference to definitions, theorems and proofs. Graduate students and scientists whose memory of specific mathematical details is dimmed may find it useful in review. Last, but not least, the authors have had in mind the adventurous student of physics and chemistry who wishes to improve his mathematical knowledge through self-study.

Henry Margenau
George M. Murphy

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March, 1943

CONTENTS

CHAPTER 1

THE MATHEMATICS OF THERMODYNAMICS

Most of the chapters of this book endeavor to treat some single mathematical method in a systematic manner. The subject of thermodynamics, being highly empirical and synoptic in its contents, does not contain a very uniform method of analysis. Nevertheless, it involves mathematical elements of considerable interest, chiefly centered about partial differentiation. Rather than omit these entirely from consideration, it seemed well to devote the present chapter to them. Of necessity, the treatment is perhaps less systematic than elsewhere. It is placed at the beginning because most readers are likely to have some familiarity with the subject and because the mathematical methods are simple. (A reading of the first chapter is not essential for an understanding of the remainder of the book.)

1.1. Introduction.—The science of thermodynamics is concerned with the laws that govern the transformations of energy of one kind into another during physical or chemical changes. These changes are assumed to occur within a *thermodynamic system* which is completely isolated from its surroundings. Such a system is described by means of *thermodynamic variables* which are of two kinds. *Extensive variables* are proportional to the amount of matter which is being considered; typical examples are the volume or the total energy of the system. Variables which are independent of the amount of matter present, such as pressure or temperature, are called *intensive variables*.

It is found experimentally that it is not possible to change all of these variables independently, for if certain ones of them are held constant, the remaining ones are automatically fixed in value. Mathematically, such a situation is treated by the method of *partial differentiation*. Furthermore, a certain type of differential, called the *exact differential* and an integral, known as the *line integral* are of great importance in the study of thermodynamics. We propose to describe these matters in a general way and to apply them to a few specific problems. We assume that the reader is familiar with the general ideas of thermodynamics and refer him to other sources[1] for a more complete treatment of the physical details.

[1] J. Williard Gibbs, Transactions of the Conn. Acad. (1875–1878); "Scientific Papers of Willard Gibbs," Vol. I., Longmans and Co. Some recent texts are: Epstein, "Textbook of Thermodynamics," John Wiley and Sons, New York, 1937; MacDougall, "Thermodynamics and Chemistry," Third Edition, John Wiley and Sons, New York, 1939; Steiner, "Introduction to Chemical Thermodynamics," McGraw-Hill Book Co., New York, 1941, Zemansky, "Heat and Thermodynamics," McGraw-Hill, N.Y., 1937.

1.2. Differentiation of Functions of Several Independent Variables.—If z is a single-valued function of two real, independent variables, x and y,

$$z = f(x,y)$$

z is said to be an *explicit function* of x and y. The relation between the three variables may be represented by plotting x, y and z along the axes of a Cartesian coordinate system, the result being a surface. If we wish to study the motion of some point (x,y) over the surface, there are three possible cases: (a) x varies and y remains constant; (b) y varies, x remaining constant; (c) both x and y vary simultaneously.

In the first and second cases, the path of the point will be along the curves produced when planes, parallel to the XZ- or YZ-coordinate planes, intersect the original surface. If x is increased by the small quantity Δx and y remains constant, z changes from $f(x,y)$ to $f(x + \Delta x,y)$, and the *partial derivative* of z with respect to x at the point (x,y) is defined by

$$f_x(x,y) = \lim_{\Delta x \to 0} \frac{f(x + \Delta x,y) - f(x,y)}{\Delta x}$$

The following alternative notations are often used

$$f_x(x,y) = z_x(x,y) = \left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \tag{1-1}$$

where the constancy of y is indicated by the subscript. Since both x and y are completely independent, the partial derivative is evaluated by the usual method for the differentiation of a function of a single variable, y being treated as a constant.

Defining the partial derivative of z with respect to y (x remaining constant) in a similar way, we may write

$$f_y(x,y) = z_y(x,y) = \left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial z}{\partial y}\right)_x \tag{1-2}$$

If z is a function of more than two variables

$$z = f(x_1,x_2, \cdots,x_n)$$

the simple geometric interpretation is lacking, but such a symbol as:

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2,x_3,\cdots,x_n}$$

still means that the function is to be differentiated with respect to x_1 by the usual rules, all other variables being considered as constants.

Since the partial derivatives are themselves functions of the independent variables, they may be differentiated again to give second and higher derivatives

$$f_{xx} = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 z}{\partial x^2}$$
$$f_{xy} = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 z}{\partial x \partial y}$$
$$f_{yx} = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 z}{\partial y \partial x} \qquad (1\text{–}3)$$
$$f_{yy} = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 z}{\partial y^2} \quad \text{etc.}$$

It is not always true that $f_{xy} = f_{yx}$; but the order of differentiation *is* immaterial if the function and its derivatives are continuous. Since this is usually the case in physical applications, quantities such as f_{xy}, f_{yx} or $f_{xxy}, f_{xyx}, f_{yxx}$ will be considered identical in the present treatment.

1.3. Total Differentials.—In the third case of sec. 1.2, both x and y vary simultaneously or, in geometric language, the point moves along a curve determined by the intersection with $z = f(x,y)$ of a surface which is neither parallel with the XZ- nor YZ- coordinate plane. Since x and y are independent, both Δx and Δy approach zero as Δz approaches zero. In that case the change in z caused by increments Δx and Δy, called the *total differential* of z, is given by

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad (1\text{–}4)$$

If it happens that x and y depend on a single independent variable u (it might be the arc length of the curve along which the point moves, or the time),

$$z = f(x,y); \quad x = F_1(u); \quad y = F_2(u)$$

then, from (4)

$$\frac{dz}{du} = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx}{du} + \left(\frac{\partial z}{\partial y}\right)_x \frac{dy}{du} \qquad (1\text{–}5)$$

For the special case,

$$z = f(x,y); \quad x = F(y); \quad y \text{ independent}$$

$$\frac{dz}{dy} = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx}{dy} + \left(\frac{\partial z}{\partial y}\right)_x \qquad (1\text{–}6)$$

An important generalization of these results arises when $x, y, \cdots$ are not independent variables but are each functions of a finite number of independent variables, $u, v, \cdots$

$$\begin{aligned} f &= f(x,y,z, \cdots) \\ x &= F_1(u,v,w, \cdots) \\ y &= F_2(u,v,w, \cdots) \\ &\cdots\cdots\cdots\cdots \end{aligned}$$

Then, from (4)

$$df = \left(\frac{\partial f}{\partial u}\right)_{v, w, \cdots} du + \left(\frac{\partial f}{\partial v}\right)_{u, w, \cdots} dv + \cdots \tag{1-7}$$

and from (5)

$$\begin{aligned} \left(\frac{\partial f}{\partial u}\right)_{v, w, \cdots} &= \left(\frac{\partial f}{\partial x}\right)_{y, z, \cdots} \left(\frac{\partial x}{\partial u}\right)_{v, w, \cdots} \\ &+ \left(\frac{\partial f}{\partial y}\right)_{x, z, \cdots} \left(\frac{\partial y}{\partial u}\right)_{v, w, \cdots} + \cdots \end{aligned} \tag{1-8}$$

with similar expressions for $(\partial f/\partial v)$, $(\partial f/\partial w)$, $\cdots$. When these are put into (7) we obtain

$$df = \left[\frac{\partial f}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial u} + \cdots\right] du + \left[\frac{\partial f}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial v} + \cdots\right] dv + \cdots$$

$$= \left[\frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv + \cdots\right]\frac{\partial f}{\partial x} + \left[\frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv + \cdots\right]\frac{\partial f}{\partial y} + \cdots \tag{1-9}$$

Since $u, v, \cdots$ are independent variables, we may write

$$\begin{aligned} dx &= \frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv + \cdots \\ dy &= \frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv + \cdots \end{aligned} \tag{1-10}$$

Comparing coefficients in (9) and (10), we finally obtain

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \cdots \tag{1-11}$$

The difference between (7) and (11) should be noted: in the former equation the partial derivatives are taken with respect to the independent variables, while in the latter, with respect to the dependent variables. The important conclusion may thus be drawn that the total differential may be written either in the form (7) or (11); that is, df may be composed additively of terms $\frac{\partial f}{\partial x} dx, \cdots$, regardless of whether x is a dependent or an independent variable.

1.4. Higher Order Differentials.—*Differentials* of the second, third and higher orders are defined by

$$d^2f = d(df); \quad d^3f = d(d^2f); \quad \cdots; \quad d^nf = d(d^{n-1}f)$$

If there are two variables x and y, we obtain from (4)

$$d^2f = d(df) = d\left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial x}\right) d(dx) + d\left(\frac{\partial f}{\partial y}\right) dy + \left(\frac{\partial f}{\partial y}\right) d(dy)$$

However,

$$d\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) dx + \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) dy = \frac{\partial^2 f}{\partial x^2} dx + \frac{\partial^2 f}{\partial x \partial y} dy$$

with a similar expression for $d\left(\frac{\partial f}{\partial y}\right)$, hence

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

If x and y are independent variables, $d^2x = d^3x = \cdots d^nx = \cdots d^ny = 0$, and the n-th order differential becomes

$$d^nf = \frac{\partial^n f}{\partial x^n} dx^n + \binom{n}{1} \frac{\partial^n f}{\partial x^{n-1} \partial y} dx^{n-1} dy + \cdots + \binom{n}{k} \frac{\partial^n f}{\partial x^{n-k} \partial y^k} dx^{n-k} dy^k$$
$$+ \cdots + n \frac{\partial^n f}{\partial x \partial y^{n-1}} dxdy^{n-1} + \frac{\partial^n f}{\partial y^n} dy^n \qquad (1\text{–}12)$$

where the $\binom{n}{k}$ are the binomial coefficients, $\binom{n}{k} = \binom{n}{n-k} = n!/k!(n-k)!$

(Cf. sec. 12.2.)

Example. Calculate dp and d^2p for a gas obeying van der Waals' equation:

$$p = \frac{RT}{V - \beta} - \frac{\alpha}{V^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V - \beta}; \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V - \beta)^2} + \frac{2\alpha}{V^3}$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0; \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V - \beta)^3} - \frac{6\alpha}{V^4}$$

$$\frac{\partial}{\partial V}\left(\frac{\partial p}{\partial T}\right) = -\frac{R}{(V - \beta)^2} = \frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)$$

$$dp = \frac{R}{(V-\beta)}\,dT + \left[\frac{2\alpha}{V^3} - \frac{RT}{(V-\beta)^2}\right]dV$$

$$d^2p = \left[\frac{2RT}{(V-\beta)^3} - \frac{6\alpha}{V^4}\right](dV)^2 - \frac{2R}{(V-\beta)^2}\,dV\,dT$$

1.5. Implicit Functions.—In the preceding discussion, the dependence of one variable on another has been given in explicit form, as $x = f(y)$. Let us assume the relation between the variables to be given in *implicit* form such as $f(x,y) = 0$. If it is now desired to compute dy/dx, one could solve $f(x,y) = 0$ for y and then differentiate. This procedure, which is often needlessly complicated, may however be avoided, for, according to (4),

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0 \tag{1-13}$$

and

$$\frac{dy}{dx} = -\frac{\left(\frac{\partial f}{\partial x}\right)_y}{\left(\frac{\partial f}{\partial y}\right)_x}$$

If the equations for a circle, $x^2 + y^2 - a^2 = 0$, or an ellipse, $x^2/a^2 + y^2/b^2 - 1 = 0$ are taken for $f(x,y) = 0$, the advantage of using this method to obtain derivatives is at once evident.

If an implicit relation is given between three variables, $F(x,y,z) = 0$, any one may be considered to depend on the other two, for there are three possible relations

$$x = f(y,z); \quad y = g(x,z); \quad z = h(x,y)$$

If x be taken as the dependent variable, then

$$dF = F_x dx + F_y dy + F_z dz = 0$$

At constant y, $dy = 0$, so that

$$\left(\frac{\partial x}{\partial z}\right)_y = -\frac{F_z}{F_x} \tag{1-14}$$

at constant z, $dz = 0$, hence

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{F_y}{F_x} \tag{1-15}$$

A third possibility arises if two relations are given between three variables

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

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

Then

$$df = f_x dx + f_y dy + f_z dz = 0$$

$$dg = g_x dx + g_y dy + g_z dz = 0$$

Solving these two equations, we obtain (see sec. 10.9)

$$dx : dy : dz = \begin{vmatrix} f_y & f_z \\ g_y & g_z \end{vmatrix} : \begin{vmatrix} f_z & f_x \\ g_z & g_x \end{vmatrix} : \begin{vmatrix} f_x & f_y \\ g_x & g_y \end{vmatrix}$$

Further examples of the properties of implicit functions and their derivatives will be found in the discussion of thermodynamic quantities.

1.6. Implicit Functions in Thermodynamics.—The simplest thermodynamic systems are homogeneous fluids or solids, subjected to no external stresses except a constant hydrostatic pressure. Investigation shows that for all such systems, there is an *equation of state* or *characteristic equation* of the form

$$f(p,V,T) = 0 \tag{1–16}$$

where p is the pressure exerted by the system, V is its volume and T, its temperature on some suitable scale. From (16), an equation of the form of (13) may then be obtained.

$$df = (\partial f/\partial p)_{V,T}\, dp + (\partial f/\partial V)_{p,T}\, dV + (\partial f/\partial T)_{p,V}\, dT = 0$$

Setting dp, dV, dT equal to zero, successively, there results a set of equations similar to (14) and (15)

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_p &= -\frac{(\partial f/\partial T)_{p,V}}{(\partial f/\partial V)_{p,T}} = \frac{1}{(\partial T/\partial V)_p} \\ \left(\frac{\partial T}{\partial p}\right)_V &= -\frac{(\partial f/\partial p)_{T,V}}{(\partial f/\partial T)_{p,V}} = \frac{1}{(\partial p/\partial T)_V} \\ \left(\frac{\partial p}{\partial V}\right)_T &= -\frac{(\partial f/\partial V)_{p,T}}{(\partial f/\partial p)_{T,V}} = \frac{1}{(\partial V/\partial p)_T} \end{aligned} \tag{1–17}$$

Three possible products may be found by multiplying any pair of these equations and removing the common terms. A typical one is

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V \tag{1–18}$$

The product of all three derivatives is

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1 \qquad (1\text{–}19)$$

These results are of considerable importance since they are verified by experiment, the derivatives being proportional to such physical quantities as the coefficients of compressibility, thermal expansion and temperature increase with pressure.

1.7. Exact Differentials and Line Integrals.—It is often required, in thermodynamic problems, to find values of a function $u(x,y)$ at two points (x_1,y_1) and (x_2,y_2) by integration of an equation

$$du(x,y) = M(x,y)dx + N(x,y)dy \qquad (1\text{–}20)$$

between the limits u_1 and u_2.

The attempted integration results in such a symbol as $\int_{x_1}^{x_2} M(x,y)dx$, which is meaningless unless y can be eliminated by a relation, $y = f(x)$. This is equivalent to specifying the path in the XY-plane along which the integration is performed, hence integrals of (20) are known as *line integrals*. There are many of these paths, the value of the definite integral differing in general, for each. The situation is particularly simple when du is a *total differential*, or, as it is often called, a *complete* or *exact differential*. Comparison of (4) with (20) shows that in this case

$$M(x,y) = \partial u/\partial x; \quad N(x,y) = \partial u/\partial y \qquad (1\text{–}21)$$

Moreover, since the order of differentiation is of no importance, it follows that

$$\partial M/\partial y = \partial^2 u/\partial x \partial y = \partial N/\partial x \qquad (1\text{–}22)$$

Inspection of (21) shows that u may be found by integration even when a functional relation between x and y is unknown. In other words, the line integral is independent of the path; it depends only on the values of x and y at the upper and lower limits. The function u is then said to be a *point function*.

In thermodynamics, it frequently happens that the upper and lower limits are the same, that is, the integration is performed around a complete *cycle*. If the differential du is exact, then the value of the line integral is zero; if du is inexact, integration around a closed cycle gives a result not equal to zero.

1.8. Exact and Inexact Differentials in Thermodynamics.—Examples of exact and inexact differentials are readily found in thermodynamics. Consider a mole of an ideal gas, whose equation of state is $pV = RT$. Let the initial conditions be V_1, p_1 and T_1 and the final conditions be V_2, p_2 and T_2. Calculate the change in volume and the work done in going

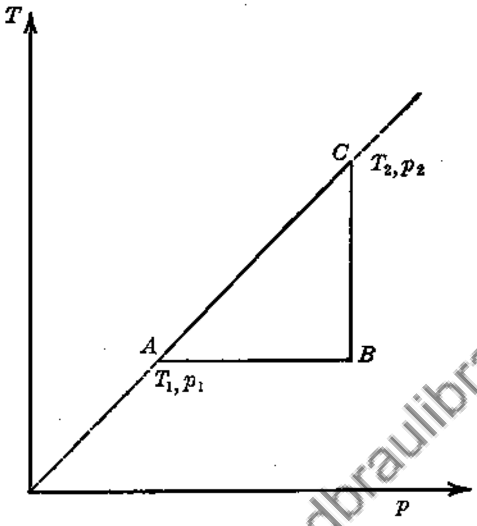

FIG. 1–1

from the initial to the final state, the integration being along two different paths in each case. Since $V = f(p,T)$,

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

$$= \frac{R}{p}\,dT - \frac{RT}{p^2}\,dp \tag{1–23}$$

Let the first equation of path (AC in Fig. 1) be

$$T - T_1 = \left(\frac{T_2 - T_1}{p_2 - p_1}\right)(p - p_1) = \frac{\Delta T}{\Delta p}(p - p_1)$$

Then $dT = \dfrac{\Delta T}{\Delta p}\,dp$ and (23) becomes

$$dV = R\left[\frac{\Delta T}{\Delta p}\frac{dp}{p} - \left(T_1 - \frac{\Delta T}{\Delta p}p_1\right)\frac{dp}{p^2} - \frac{\Delta T}{\Delta p}\frac{dp}{p}\right]$$

or, on integration,

$$V_2 - V_1 = \Delta V = \frac{R(T_2 p_1 - p_2 T_1)}{p_1 p_2}$$

The second path will be considered as consisting of two parts: AB and BC (cf. Fig. 1).

Along path AB, $T = T_1$, $dT = 0$ and along BC, $p = p_2$, $dp = 0$, hence

$$dV = -RT_1 \frac{dp}{p^2} + \frac{R}{p_2} dT,$$

or

$$\Delta V = \frac{R(T_2 p_1 - p_2 T_1)}{p_1 p_2}$$

The change in volume is thus the same for these alternative paths.

A similar conclusion might have been drawn from the test for exactness:

$$M = R/p; \quad N = -RT/p^2$$

$$\frac{\partial M}{\partial p} = -\frac{R}{p^2} = \frac{\partial N}{\partial T}$$

which shows that (23) is exact.

The mechanical work done by an expanding gas is

$$dW = pdV \tag{1-24}$$

regardless of the shape of the container and provided that the expansion is performed reversibly[2] in the thermodynamic sense. Combining (24) with (23) we obtain

$$dW = p\left(\frac{\partial V}{\partial T}\right)_p dT + p\left(\frac{\partial V}{\partial p}\right)_T dp$$

$$= RdT - \frac{RT}{p} dp \tag{1-25}$$

It is clear that dW is inexact since

$$M = R; \quad N = -\frac{RT}{p}; \quad \frac{\partial M}{\partial p} = 0 \neq \frac{\partial N}{\partial T} = -\frac{R}{p}$$

By path AC,

$$dW = R\left[dT - \left(T_1 - \frac{\Delta T}{\Delta p} p_1\right)\frac{dp}{p} - \frac{\Delta T}{\Delta p} dp\right]$$

and, on integration,

$$W_2 - W_1 = \Delta W_1 = R\left(\frac{\Delta T}{\Delta p} p_1 - T_1\right) \ln \frac{p_2}{p_1}$$

[2] Here and elsewhere in this chapter, we assume that all processes are performed reversibly when such requirement is needed for the argument. For discussions of reversibility, texts on thermodynamics should be consulted.

Along paths AB and BC,

$$dW = R\left[-T_1 \frac{dp}{p} + dT\right]$$

or

$$\Delta W_2 = R\left[-T_1 \ln \frac{p_2}{p_1} + \Delta T\right]$$

Comparison of ΔW_1 and ΔW_2 shows that the work is different along the two paths.

Heat absorbed or evolved in a process, dQ, also depends on the path. The expression for the inexact differential with p and T as independent variables is

$$dQ = \left(\frac{\partial Q}{\partial T}\right)_p dT + \left(\frac{\partial Q}{\partial p}\right)_T dp$$

$$= C_p dT + \Lambda_p dp \qquad (1\text{–}26)$$

where C_p and Λ_p are the continuous functions of T and p, known as the heat capacity at constant pressure and the latent heat of change of pressure, respectively.

Problem. Connect the points p_1, V_1 and p_2, V_2 of Fig. 1 with a circular arc. Integrate (23) along this path.

1.9. The Laws of Thermodynamics.—There are obvious advantages in expressing the laws of thermodynamics in terms of quantities which are independent of the path.[3] As we have seen, both dQ and dW are inexact, but the difference between them, a function known as the *internal energy*

$$dU = dQ - dW \qquad (1\text{–}27)$$

is an exact differential. This equation[4] often serves as a statement of the first law of thermodynamics. By combining (25) and (26) we may also write

$$dU = \left[C_p - p\frac{\partial V}{\partial T}\right] dT + \left[\Lambda_p - p\frac{\partial V}{\partial p}\right] dp \qquad (1\text{–}28)$$

with the additional requirement of exactness from (22)

$$\frac{\partial}{\partial p}\left[C_p - p\frac{\partial V}{\partial T}\right] = \frac{\partial}{\partial T}\left[\Lambda_p - p\frac{\partial V}{\partial p}\right] \qquad (1\text{–}29)$$

[3] This fact was recognized by Clausius, "The Mechanical Theory of Heat," translated by W. R. Browne, Macmillan & Co., London, 1879, who discusses the laws of thermodynamics from this standpoint.

[4] Note that $+dQ$ means heat *absorbed* and $+dW$ work *done by* the system. Minus signs indicate heat *evolved* or work *done on* the system.

These two equations are a more satisfactory definition of the first law than (27) since they show the essential fact that the internal energy, dU, is an exact differential. The inexactness of dQ and dW is sometimes indicated[5] by stating the first law in the form of (27) with symbols such as $đQ$, DQ, or δQ on the right.

The second law of thermodynamics is based upon an attempt to find a function of dQ which is an exact differential. From (27) and (24),

$$dQ = dU + dW = dU + pdV \tag{1-27a}$$

but $U = f(V,T)$, hence

$$dU = \left(\frac{\partial U}{\partial V}\right) dV + \left(\frac{\partial U}{\partial T}\right) dT$$

and

$$dQ = \left(\frac{\partial U}{\partial T}\right) dT + \left(p + \frac{\partial U}{\partial V}\right) dV \tag{1-30}$$

In passing from an initial state, V_1, T_1, to a final state, V_2, T_2, the integral on the right of (30) cannot be evaluated without further information, since the second term contains both p and V. In the special case of an ideal gas where $pV = RT$ and $(\partial U)/(\partial V)_T = 0$, (30) becomes

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \frac{RTdV}{V} \tag{1-31}$$

The first term on the right of this expression is the *heat capacity* at constant volume and depends on the temperature alone. If therefore we make the further restriction of constant temperature, that is, assume the process to be *isothermal*, the integral may be obtained. The form of (31) suggests that if we divide by T, the resulting equation

$$\frac{dQ}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{RdV}{V}$$

may also be integrated when T changes. The more general inexact differential (26) when divided by T is also exact, the quantity S so defined being the *entropy*

$$dS = \frac{dQ}{T} = \frac{C_p}{T} dT + \frac{\Lambda_p}{T} dp \tag{1-32}$$

The condition for exactness

$$\frac{\partial}{\partial p}\left(\frac{C_p}{T}\right) = \frac{\partial}{\partial T}\left(\frac{\Lambda_p}{T}\right) \tag{1-33}$$

[5] The question of a suitable notation for use in thermodynamics has been discussed by Tunell, G., *J. Phys. Chem.* **36**, 1744 (1932); *J. Chem. Phys.* **9**, 191 (1941).

together with (32) serve as basis for a statement of the *second law.* Our arguments concerning the first and second laws are intended only to show their property of exactness. The most satisfactory formulation of these laws is probably that of Carathéodory. We consider this subject in sec. 1.15.

The functions dU and dS may be combined by using (24), (27) and (32), to give

$$dU = TdS - pdV \tag{1-34}$$

Since

$$U = f(S,V) \tag{1-35}$$

and dU is exact, we may also write

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{1-36}$$

Comparison of (34) with (36) shows that

$$T = \left(\frac{\partial U}{\partial S}\right)_V ; \quad p = -\left(\frac{\partial U}{\partial V}\right)_S$$

The importance of (35) arises from the fact that if U is known as a function of two independent variables, S and V, it is possible to calculate numerical values of p, T and U for any thermodynamic state when S and V are given. A quantity like U thus furnishes more information than the equation of state, for the latter will only give p, V and T; in order to obtain U and S, the heat capacity as a function of temperature must also be given. It is not necessary to choose S and V as the independent variables in (35) or (36), in fact any pair of the set : p, V, T, S (or of the functions to be defined immediately) may be taken, but the resulting exact differential is simpler when S and V are selected.[6]

When the conditions of a specific problem suggest another pair of independent variables, it is more convenient to define additional thermodynamic functions. These are given in the following relations, where the symbol as used by Gibbs precedes the one now customary.

The *heat content* or *enthalpy*, $\chi = H = U + pV$

$$dH = dU + pdV + Vdp = TdS + Vdp \tag{1-37}$$

The *work content* or *Helmholtz free energy*, $\psi = A = U - TS$

$$dA = dU - TdS - SdT = -SdT - pdV \tag{1-38}$$

[6] Gibbs preferred S and V as independent variables for reasons given in loc. cit., footnote on page 34.

and often used. It will be described only briefly since it is a special case of a more general procedure which we give in sec. 1.13. It is unnecessary to compute the 10^{10} relations because any one of them could be obtained if the 720 first derivatives were tabulated in terms of the same set of three independent derivatives. The particular choice of the three is arbitrary, Bridgman having taken

$$\left(\frac{\partial V}{\partial T}\right)_p, \quad \left(\frac{\partial V}{\partial p}\right)_T, \quad \left(\frac{\partial Q}{\partial T}\right)_p$$

because these are directly obtainable by experiment. One could then pick any four derivatives, write them in terms of the chosen three and eliminate the three derivatives from the four equations. The result would be a single equation containing the four derivatives.

The 720 derivatives could then be classified into ten groups by holding one quantity constant and varying the other nine. Within the group containing derivatives at constant z,

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial x}{\partial w}\right)_z}{\left(\frac{\partial y}{\partial w}\right)_z} \tag{1–40}$$

which follows by writing according to (11)

$$\begin{aligned} dx &= \left(\frac{\partial x}{\partial w}\right) dw + \left(\frac{\partial x}{\partial z}\right) dz \\ dy &= \left(\frac{\partial y}{\partial w}\right) dw + \left(\frac{\partial y}{\partial z}\right) dz \end{aligned} \tag{1–41}$$

setting $dz = 0$ and dividing one equation by the other. It should be remembered that even if x and y are not functions of w and z it is still possible to have inexact differentials of the form of (41), hence the present arguments apply to dQ and dW as well as to the remaining eight thermodynamic functions. Upon adopting the abbreviations

$$\left(\frac{\partial x}{\partial w}\right)_z = (\partial x)_z$$

$$\left(\frac{\partial y}{\partial w}\right)_z = (\partial y)_z$$

any derivative at constant z may be written in purely formal fashion by taking the ratio of the proper pair, or

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{(\partial x)_z}{(\partial y)_z}$$

The task of computing the 72 derivatives in this group is thus reduced to calculation of the nine quantities $(\partial x)_z$, $(\partial y)_z$, $\cdots$. The latter are easily found when several of the derivatives $(\partial x/\partial y)_z$ are known in terms of the fundamental three for it proves possible to split the former into numerator and denominator by inspection.

If each of the remaining groups were treated in a similar way, 90 expressions of the form $(\partial x)_z$, $(\partial y)_z$, $(\partial x)_y$, $\cdots$ would be obtained but in every case $(\partial x)_y = -(\partial y)_x$ so that the final list need contain only 45 relations; they are given by Bridgman (loc. cit.) in convenient tables.[8] The following examples show their use. Let it be required to calculate $(\partial T/\partial p)_H$. From the tables, $(\partial T)_H = V - T(\partial V/\partial T)_p$, $(\partial p)_H = -C_p$, thus

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[-V + T\left(\frac{\partial V}{\partial T}\right)_p\right]$$

Many alternative forms are easily found, for example,

$$(\partial T/\partial S)_p = T/C_p; \quad (\partial T/\partial p)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p; \quad (\partial S/\partial p)_H = -V/T$$

hence,

$$\left(\frac{\partial T}{\partial p}\right)_H = \left(\frac{\partial S}{\partial p}\right)_H\left(\frac{\partial T}{\partial S}\right)_p + \left(\frac{\partial T}{\partial p}\right)_S$$

Additional examples, tables for a few of the second derivatives, and extension of the method to include mechanical variables other than pressure have also been given by Bridgman.

A further amplification of the method has been presented by Goranson[9] whose tables include the following cases: (1) one-component unit mass systems (constant total mass); (2) one-component variable mass systems or two-component unit mass systems; (3) two-component variable mass systems or three-component unit mass systems; (4) three-component variable mass systems or four-component unit mass systems. Lerman[10] has shown how the construction of such tables may be simplified.

1.11. Thermodynamic Derivatives by Method of Jacobians.—A more general method which is based on the properties of functional determinants

[8] Abbreviated tables may be found in several places, for example, Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., New York, 1939.

[9] Goranson, Roy W., "Thermodynamic Relations in Multi-component Systems," Carnegie Institution of Washington, Washington, D. C., 1930.

[10] Lerman, *J. Chem. Phys.* **5**, 792 (1937).

or Jacobians has been described by Shaw.[11] The mathematical basis on which it is founded will be discussed in detail in order to explain the construction of the required table and its application to specific examples.

1.12. Properties of the Jacobian.—The *Jacobian*[12] of x and y with respect to two independent variables, u and v, is defined by

$$J(x,y/u,v) = \partial(x,y)/\partial(u,v) = \begin{vmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix} = \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \tag{1-42}$$

When the independent variables are discernible from the context, the Jacobian may be abbreviated as $J(x,y)$, the second form of (42) being reserved for cases where it is necessary to give the independent variables explicitly. The following properties are obtained directly from the definition of the Jacobian:

$$\begin{aligned} &J(u,v) = -J(v,u) = 1; \\ &J(x,x) = 0; \quad J(k,x) = 0; \quad k, \text{ any constant} \\ &J(x,y) = J(y,-x) = J(-y,x) = -J(y,x) \end{aligned} \tag{1-43}$$

A further important property of the Jacobian arises if x and y are explicit functions of z and w, which in turn are explicit functions of u and v. Writing $\partial(x,y)/\partial(z,w)$ and $\partial(z,w)/\partial(u,v)$ in determinant form, using the rule for the multiplication of determinants, the abbreviations $(\partial x/\partial z)_w = x_z$ and so on, we have

$$\begin{vmatrix} x_z & x_w \\ y_z & y_w \end{vmatrix} \times \begin{vmatrix} z_u & z_v \\ w_u & w_v \end{vmatrix} = \begin{vmatrix} x_z z_u + x_w w_u & x_z z_v + x_w w_v \\ y_z z_u + y_w w_u & y_z z_v + y_w w_v \end{vmatrix}$$

A typical element of the product

$$x_z z_u + x_w w_u = \left(\frac{\partial x}{\partial z}\right)_w \left(\frac{\partial z}{\partial u}\right)_v + \left(\frac{\partial x}{\partial w}\right)_z \left(\frac{\partial w}{\partial u}\right)_v = \left(\frac{\partial x}{\partial u}\right)_v$$

[11] Shaw, A. N., *Phil. Trans. Roy. Soc.* (London) **A234**, 299–328 (1935).

[12] The properties of determinants, which are used here, are discussed in Chapter 10

the last form resulting from (8), hence

$$\frac{\partial(x,y)}{\partial(z,w)} \times \frac{\partial(z,w)}{\partial(u,v)} = \begin{vmatrix} x_u & x_v \\ y_u & y_v \end{vmatrix} = \frac{\partial(x,y)}{\partial(u,v)} \tag{1-44}$$

In the important special case, $y = v$,

$$\frac{\partial(x,y)}{\partial(u,y)} = \begin{vmatrix} x_u & x_y \\ y_u & y_y \end{vmatrix} = x_u y_y = \left(\frac{\partial x}{\partial u}\right)_y \tag{1-45}$$

for

$$y_y = \left(\frac{\partial y}{\partial y}\right)_x = 1 \quad \text{and} \quad y_u = \left(\frac{\partial y}{\partial u}\right)_y = 0$$

Since many thermodynamic functions are of the form $f(x,y,z) = 0$, where any one variable is determined by the other two, we may write from (4),

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

or using (45)

$$dz = \frac{\partial(z,y)}{\partial(x,y)}\, dx + \frac{\partial(z,x)}{\partial(y,x)}\, dy$$

Expressing each of these variables in terms of two new independent variables, r and s, and using the abbreviations $J(z,y) = \partial(z,y)/\partial(r,s)$, etc., (44) enables us to write

$$dz = \frac{J(z,y)}{J(x,y)}\, dx + \frac{J(z,x)}{J(y,x)}\, dy$$

If we multiply by $J(x,y)$,

$$J(z,y)dx + J(x,z)dy + J(y,x)dz = 0 \tag{1-46}$$

since $J(x,y) = -J(y,x)$, etc., from (43). If two more variables, u and v, are related to r and s in the same way, (46) may be divided by du at constant v, giving

$$J(z,y)\left(\frac{\partial x}{\partial u}\right)_v + J(x,z)\left(\frac{\partial y}{\partial u}\right)_v + J(y,x)\left(\frac{\partial z}{\partial u}\right)_v = 0$$

So that finally, again because of (45)

$$J(z,y)J(x,v) + J(x,z)J(y,v) + J(y,x)J(z,v) = 0 \qquad (1\text{–}47)$$

Problem. If r, s are functions of x, y, z and the latter in turn are functions of the independent variables u, v show that

$$J(r,s/u,v) = J(r,s/x,y)J(x,y/u,v) + J(r,s/y,z)J(y,z/u,v) + J(r,s/z,x)J(z,x/u,v).$$

1.13. Application to Thermodynamics.—This last equation is the important one which determines all of the thermodynamic partial derivatives, for if two independent variables, r and s, are chosen which completely determine the others, x, y, z, v, then any one Jacobian, for example $J(x,y)$, is given in terms of five others. But if r and s are taken from the set x, y, z, v, then $J(x,y)$ is given in terms of only four others, since by (47) $J(r,s) = \partial(r,s)/\partial(r,s) = 1$.

Let us choose p, V, T and S for x, y, z and v, respectively, so that

$$J(T,V)J(p,S) + J(p,T)J(V,S) + J(V,p)J(T,S) = 0 \qquad (1\text{–}48)$$

One more reduction is possible since from (34),

$$(\partial U/\partial V)_S = -p; \quad (\partial U/\partial S)_V = T$$

and

$$(\partial^2 U/\partial S\partial V) = (\partial T/\partial V)_S = -(\partial p/\partial S)_V$$

In Jacobian notation,

$$J(T,S)/J(V,S) = -J(p,V)/J(S,V)$$

Finally since $J(V,S) = -J(S,V)$ from (43), we obtain

$$J(T,S) = J(p,V)$$

When the following abbreviations

$$\begin{aligned} a &= J(V,T) \\ b &= J(p,V) = J(T,S) \\ c &= J(p,S) \\ l &= J(p,T) \\ n &= J(V,S) \end{aligned} \qquad (1\text{–}49)$$

are substituted into (48) and (43) is used to change the signs, we have

$$b^2 + ac - nl = 0 \qquad (1\text{–}50)$$

It is convenient to list the various Jacobians in rows and columns, $J(x,y)$ occurring at the intersection of row x with column y. The upper left-hand block of such a table is immediately filled by using the definitions (49), the rule for the change of signs, and the fact that $J(x,x) = 0$ from

(43). The entries for the lower left-hand corner of the table are obtained by writing the definitions of dU, dH, etc., in Jacobian form. For example, since

$$dU = TdS - pdV$$

$$J(U,z) = TJ(S,z) - pJ(V,z)$$

where z is any required variable. Hence, if z is taken as p and then as V

$$J(U,p) = TJ(S,p) - pJ(V,p) = -Tc + pb$$

$$J(U,V) = TJ(S,V) - pJ(V,V) = -Tn$$

the last forms following from the part of the table which is already filled or from the definitions in (49). The upper right-hand corner may be filled at the same time, without further calculation, by changing all signs. The table is completed by using relations already found, as for example

$$\begin{aligned} J(A,H) &= -J(H,A) = -SJ(T,H) - pJ(V,H) \\ &= -S(Tb - Vl) - p(Tn - Vb) \\ &= -T(Sb + pn) + V(Sl + pb) \end{aligned}$$

The final result is shown in Table 2. The use of it is typified by the following examples.

Example 1. *Evaluate $(\partial F/\partial T)_V$ in terms of other partial derivatives with T and V as independent variables.* In Jacobian notation and from Table 2

$$(\partial F/\partial T)_V = J(F,V)/J(T,V) = -\frac{Sa + Vb}{a} = -S - Vb/a$$

But

$$b/a = J(p,V)/J(V,T) = -J(p,V)/J(T,V) = -(\partial p/\partial T)_V$$

hence,

$$(\partial F/\partial T)_V = -S + V(\partial p/\partial T)_V$$

Example 2. *Transform the result of the preceding example into derivatives with p and S as independent variables.* If the previous result is used, the term a causes trouble, since with p and S as independent variables, we obtain $a = J(V,T) = \partial(V,T)/\partial(p,S)$, a relation which cannot be reduced to a single derivative. In general, as we have shown, any partial derivative may be expressed in terms of not more than three other derivatives of thermodynamic functions. We therefore use (50), which gives $a = (nl - b^2)/c$, or,

$$(\partial F/\partial T)_V = -S - Vbc/(nl - b^2)$$

TABLE 2

	p	V	T	S	U	H	A	F	Q	W
p	0	b	l	c	Tc−pb	Tc	−Sl−pb	−Sl	Tc	pb
V	−b	0	a	n	Tn	Tn−Vb	−Sa	−Sa−Vb	Tn	0
T	−l	−a	0	b	Tb+pa	Tb−Vl	pa	−Vl	Tb	−pa
S	−c	−n	−b	0	pn	−Vc	Sb+pn	Sb−Vc	0	−pn
U	−Tc+pb	−Tn	−Tb−pa	−pn	0	−TVc −p(Tn−Vb)	T(Sb+pn) +pSa	T(Sb−Vc) +p(Sa+Vb)	−pTn	−pTn
H	−Tc	−Tn+Vb	−Tb+Vl	Vc	TVc +p(Tn−Vb)	0	T(Sb+pn) −V(Sl+pb)	T(Sb−Vc) −VSl	TVc	p(Vb−Tn)
A	Sl+pb	Sa	−pa	−Sb−pn	−T(Sb+pn) −pSa	−T(Sb+pn) +V(Sl+pb)	0	SVl +p(Sa+Vb)	−T(Sb+pn)	pSa
F	Sl	Sa+Vb	Vl	−Sb+Vc	−T(Sb−Vc) −p(Sa+Vb)	−T(Sb−Vc) +VSl	−SVl −p(Sa+Vb)	0	T(Vc−Sb)	p(Sa+Vb)
Q	−Tc	−Tn	−Tb	0	pTn	−TVc	T(Sb+pn)	T(Sb−Vc)	0	−pTn
W	−pb	0	pa	pn	pTn	p(Tn−Vb)	−pSa	−p(Sa+Vb)	pTn	0

$$J(x,y) = \left(\frac{\partial x}{\partial r}\right)_s \left(\frac{\partial y}{\partial s}\right)_r - \left(\frac{\partial y}{\partial r}\right)_s \left(\frac{\partial x}{\partial s}\right)_r ; \quad b^2 + ac - nl = 0$$

But

$$b = J(p,V) = \partial(p,V)/\partial(S,p) = -(\partial V/\partial S)_p$$

$$c = J(p,S) = \partial(p,S)/\partial(S,p) = -1$$

$$l = J(p,T) = \partial(p,T)/\partial(S,p) = -(\partial T/\partial S)_p$$

$$n = J(V,S) = \partial(V,S)/\partial(S,p) = -(\partial V/\partial p)_S$$

hence,

$$(\partial F/\partial T)_V = -S - V\left[\frac{(\partial V/\partial S)_p}{(\partial T/\partial S)_p(\partial V/\partial p)_S - (\partial V/\partial S)_p^2}\right]$$

This procedure may be repeated using other quantities, such as T and S, V and p, and so on, as independent variables. The difficulty in choosing the proper form of the original relation may usually be removed in the following way. Referring to the definitions of a, b, c, l and n, it is seen that each can be reduced to unity by a proper choice of the independent variables. For example, if the latter are chosen as V and T, $a = 1$, since $a = J(V,T)$. In the previous case, $c = -1$, and it was found advisable to use some quantity other than a. The situation may be summed up in the following directions. In case one of the letters in the top line of the set $\begin{bmatrix} a & c & l & n \\ c & a & n & l \end{bmatrix}$ equals unity, do not use the one directly beneath it but transform to another by means of (50). In this way, the resulting expression will usually contain only three different partial derivatives. The omission of b from the above list arises from the fact that even if $b = 1$, only single derivatives will occur.

Example 3. *Solve for $(\partial p/\partial T)_V$ in terms of C_v, C_p and $\mu = (\partial T/\partial p)_H$, the Joule-Thomson coefficient.* Problems of this sort frequently arise where it is desired to express a partial thermodynamic derivative in terms of other quantities, which are measured directly. The usual process of obtaining the relationship is tedious and complex. From the table, it is found that

$$C_v = (\partial Q/\partial T)_V = Tn/a$$

$$C_p = (\partial Q/\partial T)_p = Tc/l$$

$$\mu = (\partial T/\partial p)_H = (Tb - Vl)/Tc$$

$$(\partial p/\partial T)_V = -b/a$$

Since there are three relations given and only two letters in the last derivative, it is convenient to write this in the form

$$(\partial p/\partial T)_V = -b^2/ab$$

and to solve for a, b and b^2 in terms of C_V, C_p and μ. Using (50) to obtain a relation between C_p and b^2, we have

$$C_p = T(nl - b^2)/al$$

$$a = Tn/C_V; \quad b^2 = la(C_V - C_p)/T; \quad b = l(\mu C_p + V)/T$$

and finally

$$(\partial p/\partial T)_V = (C_p - C_V)/(C_p\mu + V)$$

Example 4. *Determine* $(\partial U/\partial V)_T$ *for a gas obeying (i) the ideal gas law,* $pV = RT$; *(ii) van der Waals' equation,* $(p + \alpha/V^2)(V - \beta) = RT$. In problems of this sort, the resulting formulas usually contain no more than one partial derivative instead of three as in the earlier cases. From Table 2,

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{Tb}{a} - p$$

If p and V are taken as independent variables,

$$b = 1; \quad a = J(V,T) = \frac{\partial(V,T)}{\partial(p,V)} = -\left(\frac{\partial T}{\partial p}\right)_V$$

(i) $$a = -\frac{V}{R}; \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

(ii) $$a = -\frac{(V - \beta)}{R}; \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{(V - \beta)} - p = \frac{\alpha}{V^2}$$

In Shaw's paper (loc. cit.), auxiliary tables are given to simplify the calculations for the following cases: the ideal and van der Waals' gas, the saturated vapor, black-body radiation.

The Jacobian method has been extended by Shaw to include second derivatives and to apply to systems of variable composition. For these applications, as well as more detail on the use of the tables, the original paper should be consulted.[13]

Problem. Prove the following relations:

(a) $$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

(b) $$C_v - C_p = T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T$$

1.14. Thermodynamic Systems of Variable Mass.—The development of thermodynamics up to the time of Gibbs may be briefly summarized by the equation of Clausius (34) which combined the two laws. The subject

[13] The Jacobian method has also been described and illustrated with numerous examples by Sherwood, T. K. and Reed, C. E., "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Co., New York, 1939.

was thus confined to systems of *constant total mass*. Gibbs showed how this equation could be extended to include systems of variable mass.[14] If we consider a system composed of several substances whose masses are $m_1, m_2, \cdots$ we may change the internal energy not only by varying the entropy and the volume but also by varying the relative masses. Thus in place of (35) we have

$$U = U(S,V,m_1,m_2,\cdots,m_n)$$

and in place of (36)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,m_1,m_2,\cdots} dS + \left(\frac{\partial U}{\partial V}\right)_{S,m_1,m_2,\cdots} dV + \left(\frac{\partial U}{\partial m_1}\right)_{S,V,m_2\cdots} dm_1 + \left(\frac{\partial U}{\partial m_2}\right)_{S,V,m_1,\cdots} dm_2 + \cdots \tag{1-51}$$

If we write

$$\left(\frac{\partial U}{\partial m_i}\right)_{V,S,m_1,\cdots} = \mu_i \tag{1-52}$$

we have

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \cdots \tag{1-53}$$

If dU is eliminated from (53) by using in turn equations (37), (38) and (39) we obtain

$$\mu_i = \left(\frac{\partial H}{\partial m_i}\right)_{S,p,m_1,m_2,\cdots} = \left(\frac{\partial A}{\partial m_i}\right)_{V,T,m_1,m_2,\cdots} = \left(\frac{\partial F}{\partial m_i}\right)_{p,T,m_1,m_2,\cdots} \tag{1-54}$$

The partial derivatives defined by any of these equivalent expressions were called by Gibbs the *chemical potentials*. We may also convert (53) into the equation

$$dF = -SdT + Vdp + \mu_1 dm_1 + \mu_2 dm_2 + \cdots \tag{1-55}$$

At constant temperature and pressure and for a reversible process, as we have shown, $dF = 0$; hence according to (55) the condition for equilibrium reads

$$dF = \mu_1 dm_1 + \mu_2 dm_2 + \cdots = 0 \tag{1-56}$$

From this equation we may derive the celebrated *phase rule* of Gibbs. Let us understand by *phase* a homogeneous part of a system separated from the rest of the system by recognizable boundaries. Thus a mixture of ice, liquid water, and steam is a system of three phases. The number of

[14] His results also included other variables such as electric, magnetic, and gravitational fields as well as surface phenomena.

components is the least number of independently variable constituents required to express the composition of each phase. In our previous example there is only one component. In a system composed of an aqueous solution of sugar there are two components for it is necessary to specify the amounts of both water and sugar present. Finally we need a definition of *degree of freedom*. It is the number of variables (such as temperature, pressure, composition of the components) which is required to describe completely the system at equilibrium. For example, liquid water in the presence of water vapor is a system of one degree of freedom, for we may vary either the temperature or the pressure but we cannot change both simultaneously for then either the liquid or the vapor disappears.

Suppose a system contains C components and P phases, then an equation of the form of (55) will hold for each phase. Since F like S and V is an extensive variable, it follows from (55) that the chemical potentials must be independent of the masses, so that we may integrate (56) term by term obtaining

$$F = \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_C m_C \tag{1-57}$$

Differentiation of this equation results in

$$dF = \mu_1 dm_1 + \mu_2 dm_2 + \cdots + \mu_C dm_C + m_1 d\mu_1 + m_2 d\mu_2 + \cdots + m_C d\mu_C$$

When it is subtracted from (56) we get

$$m_1 d\mu_1 + m_2 d\mu_2 + \cdots + m_C d\mu_C = 0 \tag{1-58}$$

Equilibrium can be established only when an equation of this form holds for each of the P phases. But there are $C + 2$ variables T, p, μ_1, μ_2, $\cdots$, μ_C, hence the number of degrees of freedom f is

$$f = C + 2 - P \tag{1-59}$$

This simple equation has been of inestimable value in the study and interpretation of heterogeneous equilibrium by the chemist, physicist and metallurgist.[15]

1.15. The Principle of Carathéodory.—In most textbooks of thermodynamics, the order of presentation parallels the historical development of the subject. For this reason, considerable attention is paid to several kinds of ideal or imaginary machines. The customary procedure is to cite, first of all, the impossibility of constructing perpetual motion machines of various types; when this is granted it is possible to state the conditions

[15] Such applications are discussed by Findlay, A., "The Phase Rule and Its Application," Eighth Edition, Longmans, Green and Co., 1938; Desch, "Metallography," Longmans, Green and Co.

under which real machines may operate and to derive the whole body of positive assertions which are incorporated into the science of thermodynamics. The critical student may feel the need of a more logical and formal approach, and this will now be given.

We have attempted to emphasize in sec. 1.9 one important mathematical consequence of the laws of thermodynamics, namely, that functions such as dU and dS are exact differentials. We now wish to discuss a more fundamental mathematical property of these laws which was discovered by Carathéodory. His arguments[16] are derived from the geometric behavior of a certain differential equation and its solution. As a result, he is able to obtain in a purely formal way the laws of thermodynamics without recourse to fictitious machines or such objectionable concepts as the flow of heat. We cannot reproduce here the complete theory[17] but shall only give the mathematical details of his treatment of the second law.

Let us assume that a thermodynamic system is composed of n separate parts, each one of which is characterized by its pressure and volume. Further, suppose that the whole system is surrounded by adiabatic walls or thermal insulators while the individual parts of the system are separated from each other by walls that are perfect conductors of heat. As a result of experiment, it is found that there is no observable change in the system (i.e., equilibrium has been reached) when the following conditions are met:

$$f_1(p_1,V_1) = f_2(p_2,V_2) = \cdots = f_n(p_n,V_n) = F(\vartheta) \qquad (1\text{–}60)$$

The relation $f_i(p_i,V_i) = F(\vartheta)$ for the i-th part of the system is, of course, an equation of state, and ϑ is the temperature of the whole system on some suitable empirical scale. According to the first law (see eq. 27a)

$$dQ = dU + pdV = 0 \qquad (1\text{–}61)$$

the whole system being adiabatic. Moreover, a similar equation holds for each part of the system:

$$dQ_i = dU_i + p_i dV_i \qquad (1\text{–}62)$$

and

$$dU = \sum_{i=1}^{n} dU_i; \quad dQ = \sum_{i=1}^{n} dQ_i \qquad (1\text{–}63)$$

As we have shown, dQ_i is not an exact differential. However, it depends on only two variables, and under these conditions an infinite number

[16] Carathéodory, C., *Math. Ann.* **67**, 355 (1909).

[17] Carathéodory's theory has been reviewed by Born, M., *Physik. Z.* **22**, 218, 249, 282 (1922) and by Landé, A., "Handbuch der Physik," Vol. IX, Chapter 4, J. Springer, Berlin, 1926.

of integrating denominators exist.[18] Hence eq. (62) may be converted into an exact differential. Let an integrating denominator be t_i, so that

$$d\phi_i = dQ_i/t_i \tag{1-64}$$

is exact. Clearly ϕ_i is then a function of the state of the system, hence we may change (61) in such a manner that the independent variables are ϑ and ϕ_i instead of U and V. The result of this transformation is

$$dQ = \sum_{i=1}^{n}\left[\left(\frac{\partial U_i}{\partial \phi_i} + p_i\frac{\partial V_i}{\partial \phi_i}\right)d\phi_i + \left(\frac{\partial U_i}{\partial \vartheta} + p_i\frac{\partial V_i}{\partial \vartheta}\right)d\vartheta\right] = 0 \tag{1-65}$$

The quantity dQ is not exact, nor is it to be taken for granted that it can be made exact by the use of an integrating denominator if dQ contains more than two variables. As a matter of fact, the procedure is possible only when the differential equation $dQ = 0$ (known as a *Pfaff equation*) possesses a solution, as we shall show in sec. 2.18. In that case (and we shall here be interested in no other), there is an integrating denominator t such that

$$d\phi = dQ/t \tag{1-66}$$

is exact, even when there are n variables. More important for our present needs is the conclusion drawn from simple geometric considerations that if there is an integrating denominator, then there are in the neighborhood of any point P many other points which are not accessible from P along the path $dQ = 0$. This formal mathematical consequence of the properties of the Pfaff equation is known as the principle of Carathéodory. It is exactly what we need for thermodynamics. Consider, for example, a gas at a given pressure, p_1 and volume, V_1. We may expand or compress this gas adiabatically (i.e., along the path $dQ = 0$), but the final state of the system will be characterized by variables p_2, V_2 which we cannot choose at will. There are many values of p and V which we are not able to realize adiabatically.

We refer the reader again to sec. 2.18 for the conditions under which equations like (65) have a solution, hence an integrating denominator. We proceed here with the physical results which may be obtained when we know that the integrating denominator exists. In order to simplify the situation let us assume that the thermodynamic system is composed of only two parts. This restriction does not mean that there is any loss in generality of the final results since all our arguments could easily be extended to cover a system of any number of parts. With $n = 2$, it follows

[18] The proof of this fact as well as other mathematical conclusions reached here are given in sec. 2.18. Except for the proofs, the present section is complete in itself.

from (63), (64) and (66) that

$$t d\phi = t_1 d\phi_1 + t_2 d\phi_2 \tag{1-67}$$

If we take as in (65), ϕ_1, ϕ_2 and ϑ as independent variables we see that

$$\frac{\partial \phi}{\partial \phi_1} = \frac{t_1}{t}; \quad \frac{\partial \phi}{\partial \phi_2} = \frac{t_2}{t}; \quad \frac{\partial \phi}{\partial \vartheta} = 0 \tag{1-68}$$

The last equation of (68) shows that ϕ depends on ϕ_1 and ϕ_2 but not on ϑ, so that according to the other two equations of (68), the ratios t_1/t and t_2/t are also independent of ϑ:

$$\frac{\partial}{\partial \vartheta}\left(\frac{t_1}{t}\right) = 0; \quad \frac{\partial}{\partial \vartheta}\left(\frac{t_2}{t}\right) = 0$$

This result may be written:

$$\frac{1}{t_1}\frac{\partial t_1}{\partial \vartheta} = \frac{1}{t_2}\frac{\partial t_2}{\partial \vartheta} = \frac{1}{t}\frac{\partial t}{\partial \vartheta} \tag{1-69}$$

Now t_1 is a function of the state of the first member of the system and therefore could depend only on ϕ_1 and ϑ, while t_2 could depend only on ϕ_2 and ϑ. However, the first equality in (69) indicates that t_1 and t_2 must actually be functions of ϑ alone, and we may write

$$\frac{d \ln t_1}{d\vartheta} = \frac{d \ln t_2}{d\vartheta} = \frac{d \ln t}{d\vartheta} = g(\vartheta) \tag{1-70}$$

where $g(\vartheta)$ is a function which is common to all systems in thermal contact, not dependent on any special properties of the substances which compose the system. Integrating (70), we obtain

$$\ln t = \int g(\vartheta) d\vartheta + \ln A(\phi) \tag{1-71}$$

where the integration constant $\ln A$ depends only on the quantity ϕ. Note that we have dropped the subscripts from t and ϕ so that eq. (71) refers to any thermodynamic system and t is the appropriate integrating denominator for the particular system under consideration. We see from (71) the important fact that this denominator can be separated into two parts, one depending only on the empirical temperature ϑ and the other only on variables of the state of the system such as ϕ whose differential is exact.

Let us rewrite (71) in the form

$$t = A e^{\int_a^\vartheta g(\vartheta) d\vartheta} \tag{1-72}$$

and define the *absolute temperature* T by the relation

$$T(\vartheta) = Ce^{\int g(\vartheta)d\vartheta} \tag{1-73}$$

The constant C relating ϑ and T may be determined by requiring that between two fixed points, say the boiling point and freezing point of water, T shall increase by 100 units. It should be noticed that there is no additive constant in (73), so that if C is positive, the smallest value of T is zero, and there is no upper limit for T.

If our thermodynamic system contains only one part, we may use (72), (73) and (66) to write

$$dQ = td\phi = \frac{TAd\phi}{C} \tag{1-74}$$

Also, if we put

$$S = \frac{1}{C}\int A(\phi)d\phi + \text{const.} \tag{1-75}$$

we obtain the well-known expression for the second law of thermodynamics which defines a change in entropy, dS:

$$dQ = TdS \tag{1-76}$$

The entropy is immediately seen to be a function of the state of the system, constant along an adiabatic path ($dQ = 0$). It is determined except for an additive constant. We also note from (76) that the absolute temperature is an integrating denominator of the inexact differential dQ.

When the system is made up of two parts which are in thermal contact, eqs. (67) and (74) may be combined to give

$$Ad\phi = A_1d\phi_1 + A_2d\phi_2 \tag{1-77}$$

We know that A_1 is a function of ϕ_1 and that A_2 is a function of ϕ_2. We want to prove that A is a function of ϕ which in turn depends on ϕ_1 and ϕ_2. Let us *assume* that $A = A(\phi)$. Then

$$\frac{\partial A}{\partial \phi_1} = \frac{\partial A}{\partial \phi}\frac{\partial \phi}{\partial \phi_1}; \quad \frac{\partial A}{\partial \phi_2} = \frac{\partial A}{\partial \phi}\frac{\partial \phi}{\partial \phi_2}$$

If we eliminate $\partial A/\partial\phi$ from these two equations we obtain

$$\frac{\partial A}{\partial \phi_1}\frac{\partial \phi}{\partial \phi_2} - \frac{\partial A}{\partial \phi_2}\frac{\partial \phi}{\partial \phi_1} = 0 \tag{1-78}$$

This result is often written in the Jacobian notation of sec. 1.12

$$J(A,\phi/\phi_1,\phi_2) = 0$$

It tells us[19] that if A is a function of ϕ, $J(A,\phi) = 0$ and conversely if $J(A,\phi) = 0$, then A is a function of ϕ. We can easily prove in our case that the Jacobian does vanish. Differentiation of (77) results in

$$A \frac{\partial \phi}{\partial \phi_1} = A_1, \quad A \frac{\partial \phi}{\partial \phi_2} = A_2$$

$$\frac{\partial A}{\partial \phi_1} \frac{\partial \phi}{\partial \phi_2} + A \frac{\partial^2 \phi}{\partial \phi_1 \partial \phi_2} = 0; \quad \frac{\partial A}{\partial \phi_2} \frac{\partial \phi}{\partial \phi_1} + A \frac{\partial^2 \phi}{\partial \phi_2 \partial \phi_1} = 0$$

hence by subtraction we obtain (78). Thus A is a function of ϕ. Under these conditions we have an equation similar to (76) for each part of the thermodynamic system, and since $dQ = \sum dQ_i$, we finally conclude from (75) and (77) that $dS = \sum dS_i$.

[19] This result which may be applied in the case of n variables is often useful. If the n functions $y_1, y_2, \cdots, y_n$ are not independent of each other the Jacobian vanishes; if $J = 0$, then the n functions are related by some equation $f(y_1, y_2, \cdots, y_n) = 0$.

CHAPTER 2

ORDINARY DIFFERENTIAL EQUATIONS

2.1. Preliminaries.—The customary classification distinguishes two main types: *ordinary* and *partial* differential equations. The former contain only one independent variable and, as a consequence, total derivatives. They represent a relation between the primitive of the dependent variable (y), its various derivatives, and functions of the independent variable (x). Partial differential equations, whose study will be reserved for Chapter 7, contain several independent variables and hence partial derivatives. Concerning terminology, the following is to be noted in connection with ordinary differential equations.

The *order* of a differential equation is the order of its highest derivative; its *degree* is the degree (or power) of the derivative of highest order after the equation has been rationalized, i.e., after fractional powers of all derivatives have been removed. Thus the equation

$$\frac{d^2y}{dx^2} + \left(\frac{dy}{dx}\right)^2 + xy = 0$$

is of the second order and the first degree, while

$$\frac{d^2y}{dx^2} + \sqrt{\frac{dy}{dx}} + xy = 0$$

is of the second order and the second degree. If the dependent variable and all its derivatives occur in the first degree and not multiplying each other, the equation is said to be *linear*. The solution of an equation of n-th order involves, in principle, the carrying out of n quadratures or integrations. Since each of them introduces one arbitrary constant, the final expression for the dependent variable will contain n arbitrary constants. However, a solution in which one or more of these constants are given specific values, for instance the value zero, will also satisfy the differential equation. In view of this consideration two types of solutions of an ordinary differential equation of n-th order may be distinguished: (1) the *complete* or *general* solution which contains its full complement of n independent[1] arbitrary constants; (2) *particular* solutions, obtainable from the general one by fixing one or more of the constants. In addition to these, differential equations of degree higher than the first frequently possess solutions, known as *singular* ones, which cannot be formed from the general solution in this manner. An example of these will be discussed briefly in sec. 2.6; they are rarely of interest in physical or chemical applications.

FIRST ORDER EQUATIONS

An equation of the first order can always be solved although the solution may sometimes not be expressible in terms of familiar or named functions. Methods of solution applicable in the most frequently occurring cases will now be given, and the discussion of each method will be followed by a list of problems, arising in physics and chemistry, which lead to differential equations solvable by the scheme in question.

2.2. The Variables are Separable.—This is true when the equation, which may originally appear in the form $f_1(x,y)\dfrac{dy}{dx} + f_2(x,y) = 0$, is reducible to

$$f(x)dx + g(y)dy = 0$$

Such an equation can be integrated at once and leads to a relation between y and x.

Examples.

a. *Organic growth; radioactive decay.*

Bacterial cultures in an unlimited nutritive medium grow at a time rate proportional to the number of bacteria present at any moment. Hence if the time t is regarded as independent variable and N, the number of bacteria present at time t as dependent variable,

$$\frac{dN}{dt} = \alpha N$$

α being the rate of growth per bacterium. This may be written

$$\frac{dN}{N} = \alpha dt$$

[1] Arbitrary constants are said to be independent if two or more of them cannot be replaced by an equivalent single one. Thus the constants c_1 and c_2 in the functions: $ax + c_1 + c_2$ and $c_1e^{x+c_2}$ are not independent because these functions may be written $ax + c$ and ce^x, respectively.

This distinction is elementary. A more adequate analysis would focus attention upon independent *solutions* of the differential equation rather than independent constants. Solutions are independent when the so-called *Wronskian* determinant fails to vanish. This matter is treated in sec. 3.13.

which, on integration, yields $\ln N = \alpha t + c$, or $N = Ce^{\alpha t}$. If the original number of bacteria at $t = 0$ is N_0, the constant C must have the value N_0 to conform to this physical condition.

Radioactive atoms decay at a rate proportional to the number of atoms, N, present at any moment, t. Hence $dN/dt = -\lambda N$, which has the solution $N = N_0 e^{-\lambda t}$. The disintegration constant λ measures the time rate of decay per atom. It is a fundamental quantity characteristic of each radioactive substance.

b. *Flow of water from an orifice.*

A vertical tank of uniform cross-section A is filled with water to an initial height h_0. Water flows out through a hole of area a. It is desired to find the height of the water, h, in the tank as a function of the time, t. The volume flowing out in time dt is $avdt$, where v is the velocity of the water at the orifice at time t. The loss of height in the tank is dh, hence the loss of volume Adh. Therefore

$$avdt = -Adh$$

But the velocity is related to the height by Torricelli's formula: $v = c\sqrt{2gh}$. The empirical constant c would be unity if there were no obstruction and no "vena contracta" near the orifice; for ordinary small holes with sharp edges it is 0.6. Thus

$$ac\sqrt{2gh}dt = -Adh$$

or

$$\frac{dh}{\sqrt{h}} = -c\frac{a}{A}\sqrt{2g}dt$$

On integrating this we have

$$\sqrt{h} = \sqrt{h_0} - \frac{c}{2}\frac{a}{A}\sqrt{2g}t$$

where the constant of integration has been so adjusted that $h = h_0$ at $t = 0$.

c. *Heat flow.*

When heat flows through a body the temperature, T, is in general a complicated function of the coordinates within the body. In simple cases, however, it may depend only on a single coordinate, x (distance from a heated plane, or distance from a point source of heat). In that case, the rate at which heat crosses an area A perpendicular to x is given by

$$R = -kA\frac{dT}{dx} \tag{2–1}$$

and R is constant because of the continuity of flow. The quantity k is known as the thermal conductivity.

(α) If the body is a slab with plane parallel faces, one of which is maintained at a temperature T_1, integration of (1) leads to

$$T_1 - T = \frac{Rx}{kA}$$

x being the distance from the heated face. From this one obtains the elementary relation

$$R = kA\,\frac{T_1 - T_2}{d} \tag{2-2}$$

for the heat transfer across a plate of thickness d.

(β) If a heat source is placed at the center of a sphere, the temperature is a function of r alone. Here $A = 4\pi r^2$, and (1) reads $-4\pi kr^2(dT/dr) = R$, which gives

$$T = \frac{1}{4\pi k}\,\frac{R}{r} + C$$

In this case, the temperature is not a linear function of the distance from the source as it was in (α).

(γ) At constant external temperature the thickness of ice on quiescent water increases as the square root of the time. To show this we write (2) in the form

$$R \equiv \frac{dH}{dt} = kA\,\frac{\Delta T}{x}$$

where x now represents the thickness of ice and dH the quantity of heat transported away from the lower surface of the ice in time dt. This, however, is proportional to the thickness dx which is added on to the already existing layer in time dt. Hence $dx/dt = C/x$, C representing a constant. From this it follows by integration that

$$x^2 \sim t$$

d. *Salt dissolving in water.*

When x_0 grams of salt are placed in M grams of water at time $t = 0$, how many grams will remain undissolved at time t? The rate of solution, dx/dt, is proportional, (a) to the number of grams, x, undissolved at time t, (b) to the difference between the saturation concentration, X/M, and the actual concentration, $(x_0 - x)/M$. (X is the number of grams of salt that would produce saturation.) Thus

$$-\frac{dx}{dt} = kx \cdot \left(\frac{X}{M} - \frac{x_0 - x}{M}\right) = \frac{k}{M}\,[(X - x_0)x + x^2] \tag{2-3}$$

To solve, we write

$$-\frac{dx}{(X-x_0)x+x^2} = -\frac{1}{X-x_0}\left(\frac{dx}{x} - \frac{dx}{X-x_0+x}\right) = \frac{k}{M}\,dt$$

Integration then leads to: $\ln\frac{X-x_0+x}{x} + c = \frac{X-x_0}{M}\,kt$. When the constant c is adjusted so that $x = x_0$ at $t = 0$, the result is

$$\ln\frac{(X-x_0+x)x_0}{xX} = \frac{X-x_0}{M}\,kt$$

If $x_0 = X$, then the solution is $\frac{1}{x} - \frac{1}{x_0} = (k/M)t$, as one may easily verify by going back to equation (3).

e. *Atmospheric pressure at any height.*

The increment of pressure between two points in the atmosphere differing in height by dh is $dP = -\rho g dh$, if ρ is the density at height h. But ρ is related to P by the expression $P\rho^{-\gamma} = P_0\rho_0^{-\gamma}$, which is valid for adiabatic expansion of air if γ is taken to be 1.4.[2] The quantities P_0 and ρ_0 are the sea level values of P and ρ. Therefore

$$dP = -\left(\frac{P}{P_0}\right)^{1/\gamma} \rho_0 g dh$$

and this, on integration, gives $\left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}} = 1 - \frac{\gamma-1}{\gamma}\frac{\rho_0 g h}{P_0}$, the constant of integration being adjusted so that $P = P_0$ at $h = 0$.

f. *Homogeneous gas reactions.*

Chemical reactions involving but a single phase are said to be homogeneous. Among these there may be distinguished unimolecular, bimolecular, termolecular reactions and so on. In the unimolecular case, the number of molecules undergoing a chemical change is at any instant proportional to the number of molecules present. The decomposition of nitrogen pentoxide into oxygen and nitrogen tetroxide ($2N_2O_5 \rightarrow O_2 + N_2O_4$) is an example of this kind, the differential equation being similar to that describing radioactive decay (Example a).

In a bimolecular reaction, of which there are numerous examples, substances A and B form molecules of type C. If a and b are the original concentrations of A and B respectively, and x is the concentration of C at a given instant, then

$$\frac{dx}{dt} = k(a-x)(b-x)$$

[2] γ is the ratio of the specific heat at constant pressure to that at constant volume.

To integrate this equation, the expression $\frac{1}{(a-x)(b-x)}$ is resolved into the partial fractions $\frac{1}{a-b}\left[\frac{1}{b-x}-\frac{1}{a-x}\right]$. We then have

$$\frac{1}{a-b}\int\left(\frac{dx}{b-x}-\frac{dx}{a-x}\right)=\int kdt$$

whence

$$\frac{1}{a-b}\ln\frac{a-x}{b-x}=kt+c$$

Since $x = 0$ at $t = 0$, $c = \frac{1}{a-b}\ln\frac{a}{b}$, so that

$$\frac{b(a-x)}{a(b-x)}=e^{(a-b)kt}$$

From this, the *reaction rate* is seen to be

$$k=\frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

The concentration of substance C is

$$x=\frac{a(1-e^{(a-b)kt})}{\left(1-\frac{a}{b}e^{(a-b)kt}\right)}$$

When the original concentrations a and b are equal, the expression for k becomes indeterminate, but on putting $b = a + \epsilon$ and letting ϵ approach zero, an expansion of the logarithm yields

$$k=\frac{1}{at}\frac{x}{a-x}$$

which is also seen to be a solution of the differential equation

$$\frac{dx}{dt}=k(a-x)^2$$

Other types of reactions will be dealt with in the problems on p. 40. As to terminology, we note that a rate law for multimolecular reactions of the form

$$\frac{dx}{dt}=k(a_1-x)^{n_1}(a_2-x)^{n_2}\cdots(a_s-x)^{n_s}$$

is often said to describe a reaction of the n-th order, where

$$n=\sum_1^s n_i$$

g. *Clapeyron's equation.*

Any phase change of a substance which takes place at constant pressure and temperature conforms to Clapeyron's equation:

$$\frac{dP}{dT} = \frac{l}{T(V_f - V_i)}$$

Here l represents the latent heat of the process, V_f and V_i the volume per mole of the final and the initial phase respectively, and P the pressure. This equation may be applied to the process of sublimation, yielding an approximate expression for the vapor pressure as a function of the temperature. In that case l, the latent heat of sublimation of the solid, is nearly constant over a range of temperatures, and V_i, the volume of the solid, may be neglected in comparison with that of the vapor, V_f. The vapor, though not a perfect gas, will be taken to satisfy $V_f = RT/P$. Clapeyron's equation then becomes

$$\frac{dP}{dT} = \frac{lP}{RT^2}$$

which on integration gives

$$P = ce^{-l/RT}$$

an equation often called the Clausius-Clapeyron equation. This result is found to be valid over small ranges of temperature, for the vapor pressure of both solids and liquids. A more refined result may be obtained by introducing for l a more adequate approximation.

h. *Centrifuge problem.*

When a cylinder of height h, filled with fluid, is rotating about its axis, the pressure within the fluid will not be constant but will depend on r. Consider a cylindrical shell of fluid of thickness dr, the surfaces of which are coaxial with the rotating vessel. The net force pushing inward on this shell is $2\pi rhdP$. This must equal the centripetal force due to the angular speed ω, namely $m\omega^2 r$, where m, the mass of the fluid, is given by $2\pi rhdr \cdot \rho$. Hence

$$2\pi rhdP = 2\pi rh\rho dr \cdot \omega^2 r$$

(α) If the fluid is a liquid, the density, ρ, is constant and the solution is

$$P = \tfrac{1}{2}\rho\omega^2 r^2 + P_0$$

(β) If the fluid is a gas, $P = c\rho$ (since PV = const.), the solution is then

$$P = P_0 e^{\omega^2 r^2/2c}$$

i. *Soap film.*

If a soap film is stretched between two circular wires, both having their planes perpendicular to the line joining their centers, it will form a figure of revolution about that line. At every point such as P (cf. Fig. 1) the horizontal force acting around a vertical section of the film is the same. Hence

$$2\pi y T \cos\theta = \text{const.}$$

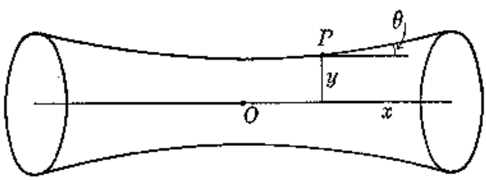

FIG. 2–1

where T is the surface tension of the film. But

$$\cos\theta = \left[1 + \left(\frac{dy}{dx}\right)^2\right]^{-1/2}$$

so that

$$y\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{-1/2} = c$$

T being a constant. Solving for the derivative,

$$\frac{dy}{dx} = \left(\frac{y^2}{c^2} - 1\right)^{1/2}$$

which leads to

$$y = c \cosh\frac{x + c_1}{c}$$

The constants c and c_1 may be expressed in terms of the distance between the wires and their radius. The longitudinal section of the film is seen to be a catenary.

The examples above seem sufficient to illustrate the method under discussion. The problems leading to separable first order equations are very numerous.

Problems.

a. *Helmholtz' equation.*

If a circuit has resistance R and inductance L, the current I in it obeys the differential equation

$$L\frac{dI}{dt} + RI = E$$

where E is the impressed or external electromotive force. Show that the *growth* of a current (E = const., $I = 0$ at $t = 0$) is described by

$$I = \frac{E}{R}\left(1 - e^{-(R/L)t}\right)$$

and the *decay* ($E = 0$, $I = I_0$ at $t = 0$) by

$$I = I_0 e^{-(R/L)t}$$

b. Solve the equation for *termolecular reactions:*

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x).$$

Ans.
$$\left(1 - \frac{x}{a}\right)^{c-b}\left(1 - \frac{x}{b}\right)^{a-c}\left(1 - \frac{x}{c}\right)^{b-a} = e^{(c-b)(a-c)(b-a)kt}$$

c. Solve the equation for *opposing unimolecular and bimolecular reactions:*

$$\frac{dx}{dt} = k_1(a - x) - k_2x^2$$

under the condition $x = 0$ at $t = 0$.

Ans.
$$\frac{a}{x} = \frac{k_2}{k_1} A \coth Ak_2t + \tfrac{1}{2} \quad \text{where} \quad A^2 = \frac{k_1}{k_2}\left(a + \frac{1}{4}\frac{k_1}{k_2}\right)$$

Show that, when equilibrium is established ($t = \infty$),

$$\frac{x^2}{a - x} = \frac{k_1}{k_2}$$

d. Solve the equation for *consecutive unimolecular reactions* of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

that is,

$$\frac{dn_1}{dt} = -k_1n_1, \quad \frac{dn_2}{dt} = k_1n_1 - k_2n_2$$

Ans.
$$n_3 = (n_1 + n_2 + n_3)\left\{1 - \frac{k_2}{k_2 - k_1} e^{-k_1t} + \frac{k_1}{k_2 - k_1} e^{-k_2t}\right\}$$

where n_3 = amount of C present at t.

e. A projectile is fired vertically into the air with initial velocity V. (1) Find its speed at any height; (2) find the time at which it will have traversed a distance . Note: the differential equation to be solved is

$$\frac{dv}{dt} \equiv v\frac{dv}{dr} = -\frac{gR^2}{r^2}$$

where g = acceleration due to gravity, R = radius of the earth.

Ans. (1)
$$v = \left[V^2 - 2gR\left(1 - \frac{R}{r}\right)\right]^{1/2}$$

(2) If $V^2 > 2gR$

$$t = (V^2 - 2gR)^{-1}\left\{\left[\left(V^2 - 2gR + \frac{2gR^2}{r}\right)^{1/2} - V\right]r - \frac{2gR^2}{(V^2 - 2gR)^{1/2}}\left[\ln \frac{\left(V^2 - 2gR + \frac{2gR^2}{r}\right)^{1/2} + (V^2 - 2gR)^{1/2}}{V + (V^2 - 2gR)^{1/2}} + \tfrac{1}{2}\ln\frac{r}{R}\right]\right\}$$

2.3. The Differential Equation is, or Can be Made, Exact. Linear Equations.—A differential equation, written in the form

$$A dx + B dy = 0 \qquad (2\text{–}4)$$

where A and B are functions of x and y, is said to be exact if the left-hand side is an exact differential. The necessary and sufficient condition for this to be true was shown in sec. 1.7 to be equivalent to the *Cauchy relations*

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$$

The equations considered in the foregoing section, where A was a function of x alone and B a function of y alone, are exact in the trivial sense that $\partial A/\partial y = \partial B/\partial x = 0$.

Differential equations occurring in practice are rarely exact, but every equation of the form (4) can be made exact and then integrated. The device for doing this is to multiply it by a suitable factor known as the *integrating factor*. For instance, the equation

$$\frac{dy}{y} + \left(\frac{1}{x} - \frac{x}{y}\right) dx = 0$$

is not exact. It becomes exact on multiplication by xy. For it then takes the form

$$d\left(xy - \frac{x^3}{3}\right) = 0$$

which has the solution:

$$xy - \frac{x^3}{3} = \text{const.}$$

While an integrating factor exists for every equation of the form (4), it is not always easy to find. If the equation is *linear*, however, that is if it can be written

$$\frac{dy}{dx} + f(x)y = g(x) \qquad (2\text{–}5)$$

an integrating factor is always available. It is $e^{\int f dx}$. On application of this factor eq. (5) becomes

$$\frac{d}{dx}(ye^F) = g(x)e^F$$

where the abbreviation $F(x) = \int^x f(\xi)d\xi$ has been used. The solution is, clearly,

$$y = e^{-F}\left[\int e^F g dx + c\right] \tag{2-6}$$

This result is most useful, for the occurrence of linear equations is very frequent.

Examples.

a. *Circuit containing inductance and resistance* (Helmholtz' equation). This problem has already been discussed, but it may be instructive to solve the differential equation also by the method of eq. (6). We have

$$\frac{dI}{dt} + \frac{RI}{L} = \frac{E}{L} \tag{2-7}$$

Thus

$$f = \frac{R}{L} \quad \text{and} \quad F = \frac{R}{L}t; \quad g = \frac{E}{L}$$

so that

$$I = e^{-(R/L)t}\left[\int \frac{E}{L} e^{(R/L)t}dt + c\right] = \frac{E}{R} + ce^{-(R/L)t}$$

and this agrees with our previous result (Problem a).

b. *Circuit with inductance and resistance; variable electromotive force.* The present method involves the solution of eq. (7) when E is a function of the time, in which case the equation can no longer be separated. Let us assume that

$$E = E_0 \sin \omega t$$

We then have

$$f = \frac{R}{L}; \quad F = \frac{R}{L}t; \quad g = \frac{E_0}{L}\sin \omega t$$

Hence[3]

$$I = \frac{e^{-(R/L)t}}{L} E_0 \int e^{(R/L)t} \sin \omega t dt + ce^{-(R/L)t}$$

$$= \frac{E_0}{L} \frac{1}{\omega'^2 + \omega^2} (\omega' \sin \omega t - \omega \cos \omega t) + ce^{-(R/L)t}$$

where ω' has been written for R/L, a quantity having the dimensions of a frequency. To fix the constant we assume that $I(0) = 0$, in which case

$$I = \frac{E_0}{L} \frac{1}{\omega'^2 + \omega^2} (\omega' \sin \omega t - \omega \cos \omega t + \omega e^{-\omega' t})$$

The last term represents transient currents which disappear as soon as $t \gg \frac{1}{\omega'}$.

c. *Radioactive decay of mother and daughter substances.*

Let A be the number of atoms of the mother substance (e.g., UI) and B the number of atoms of the daughter substance (e.g., UX_1) at time t, A_0 being the original value of A at $t = 0$. Let λ_A and λ_B be the decay constants as defined in sec. 2.2a. The two substances satisfy the two differ-

[3] Here and elsewhere, there occurs the integral $\int e^{\omega' t} \sin \omega t dt$. This is easily evaluated if the sine is written as an exponential:

$$\sin x = \frac{1}{2i} (e^{ix} - e^{-ix}).$$

Thus

$$\int e^{\omega' t} \sin \omega t dt = \frac{1}{2i} \int [e^{(\omega'+i\omega)t} - e^{(\omega'-i\omega)t}] dt$$

$$= \frac{1}{2i} \left\{ \frac{e^{(\omega'+i\omega)t}}{\omega' + i\omega} - \frac{e^{(\omega'-i\omega)t}}{\omega' - i\omega} \right\} = \frac{e^{\omega' t}}{2i} \left\{ \frac{(\omega' - i\omega)e^{i\omega t} - (\omega' + i\omega)e^{-i\omega t}}{\omega'^2 + \omega^2} \right\}$$

$$= \frac{e^{\omega' t}}{\omega'^2 + \omega^2} (\omega' \sin \omega t - \omega \cos \omega t) = -\frac{e^{\omega' t}}{(\omega'^2 + \omega^2)^{1/2}} \cos (\omega t + \beta)$$

$$\beta = \tan^{-1} \frac{\omega'}{\omega}.$$

Similarly:

$$\int e^{\omega' t} \cos \omega t dt = \frac{e^{\omega' t}}{\omega'^2 + \omega^2} (\omega' \cos \omega t + \omega \sin \omega t)$$

$$= \frac{e^{\omega' t}}{(\omega'^2 + \omega^2)^{1/2}} \sin (\omega t + \beta)$$

ential equations

$$\frac{dA}{dt} = -\lambda_A A; \quad \frac{dB}{dt} = -\lambda_B B + \lambda_A A$$

When the solution of the first, $A = A_0 e^{-\lambda_A t}$, is substituted in the second there results

$$\frac{dB}{dt} + \lambda_B B = \lambda_A A_0 e^{-\lambda_A t}$$

an equation which is linear in B and can be solved by formula (6). The solution is:

$$B = e^{-\lambda_B t}\left\{\int \lambda_A A_0 e^{(\lambda_B - \lambda_A)t} dt + c\right\}$$

$$= \frac{\lambda_A}{\lambda_B - \lambda_A} A_0 (e^{-\lambda_A t} - e^{-\lambda_B t})$$

if we assume that $B(0) = 0$. Note that B will reach a maximum at time $t = \dfrac{\ln \lambda_A - \ln \lambda_B}{\lambda_A - \lambda_B}$.

Problem. A circuit contains capacitance C, resistance R, and is subject to an electromotive force E. Calculate the instantaneous value of the electric charge q on the condenser, noting that it satisfies the differential equation

$$R\frac{dq}{dt} + \frac{q}{C} = E$$

Ans. For $E = E_0 \sin \omega t$,

$$q = \frac{E_0}{R}\frac{1}{\omega'^2 + \omega^2}(\omega' \sin \omega t - \omega \cos \omega t + \omega e^{-\omega' t}), \quad \omega' = \frac{1}{RC}$$

2.4. Equations Reducible to Linear Form.—Of some mathematical interest is an equation of the form

$$\frac{dy}{dx} + f(x)y = g(x)y^n \tag{2-8}$$

because it can be made linear by the substitution $y = u^{1/1-n}$. This converts (8) into

$$\frac{du}{dx} + (1 - n)fu = (1 - n)g$$

which can be solved by the method of the preceding section. Eq. (8) is often called Bernoulli's equation.

2.5. Homogeneous Differential Equations.—A first order equation is said to be homogeneous[4] if, the equation being written in the form

$$A\,dx + B\,dy = 0$$

A and B are homogeneous functions of the same degree, i.e.,

$$A(tx,ty) = t^{\alpha}A(x,y); \quad B(tx,ty) = t^{\alpha}B(x,y)$$

If this is true we can substitute $y = vx$, obtaining

$$A(x,y) = A(x,vx) = x^{\alpha}A(1,v); \quad B(x,y) = x^{\alpha}B(1,v)$$

The original equation,

$$\frac{dy}{dx} = -\frac{A}{B}$$

is converted into

$$v + x\frac{dv}{dx} = -\frac{A(1,v)}{B(1,v)} \equiv f(v)$$

by this substitution, and this equation is separable, yielding

$$\frac{dv}{f(v) - v} = \frac{dx}{x}$$

Example. *Lines of force.*

An equation closely related to the homogeneous type, and tractable by the

[4] A remark on the use of the word "homogeneous" in mathematics seems in order, for the term is used with several different meanings in different contexts. The following definitions correspond to the chief usages.

1. Homogeneous function: $f(x_1,x_2,\cdots x_n)$ is said to be homogeneous in all its variables if, for any parameter, t, $f(tx_1,tx_2,\cdots tx_n) = t^{\alpha}f(x_1,x_2,\cdots x_n)$. α is the "degree" of the homogeneous function.

2. Homogeneous equations: A set of simultaneous linear algebraic equations of the form

$$\sum_{i=1}^{n} a_{ji}x_i = c_j; \quad j = 1, 2, \cdots, n$$

in which the a's are constants is said to be homogeneous if all c's are zero.

3. Homogeneous differential equations: (Two usages of the term!)

a. A first order equation of the form $A\,dx + B\,dy = 0$ is said to be homogeneous if $A(x,y)$ and $B(x,y)$ are homogeneous functions of the same degree.

b. In general, $F(x,y,y',y'',\cdots) = 0$ is said to be homogeneous if F is a homogeneous function of y and all its derivatives, *not necessarily of x.* Thus

$$f_n(x)\frac{d^n y}{dx^n} + f_{n-1}(x)\frac{d^{n-1}y}{dx^{n-1}} + \cdots f_1(x)\cdot y = 0$$

is homogeneous and linear. If the right-hand side of this equation were not zero but equal to a function of x, the equation would still be linear but no longer homogeneous.

substitution here described, is the differential equation for lines of force. A line of force is defined as that curve which is tangent, at every point through which it passes, to the force at that point. The present analysis is applicable to attracting mass points, attracting or repelling electric

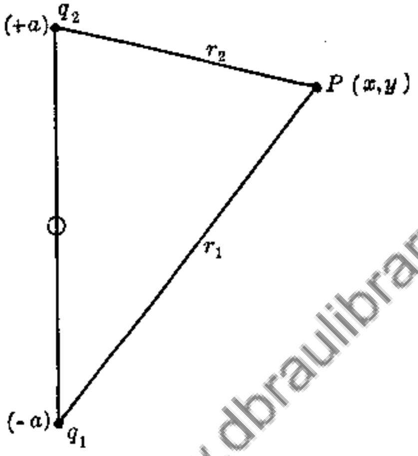

Fig. 2–2

charges, and magnetic poles. Let it be desired, for example, to find the lines of force due to two charges, q_1 and q_2, a distance $2a$ apart. (Cf. Fig. 2.) If we restrict our consideration to the plane containing the charges and the point P, then, for every point in this plane, the definition of a line of force requires that

$$\frac{dy}{dx} = \frac{F_y}{F_x} = \frac{\dfrac{q_1}{r_1^3}(y + a) + \dfrac{q_2}{r_2^3}(y - a)}{\dfrac{q_1}{r_1^3}x + \dfrac{q_2}{r_2^3}x} \tag{2–9}$$

If a were zero, this would reduce to $dy/dx = y/x$, an equation which has for its solution all straight lines through the origin. These, as is well known, represent the lines of force due to a point charge. In general however, eq. (9) reads

$$\frac{q_1}{r_1^3}[xdy - (y + a)dx] + \frac{q_2}{r_2^3}[xdy - (y - a)dx] = 0 \tag{2–9a}$$

This equation misses being homogeneous by the presence of the quantity a. But a simple artifice will help. If we introduce two new dependent variables, $y_1 = y + a$ and $y_2 = y - a$, so that $dy_1 = dy_2 = dy$; $r_1 = (x^2 + y_1^2)^{1/2}$, $r_2 = (x^2 + y_2^2)^{1/2}$, eq. (9a) takes the form

$$q_1 \frac{x dy_1 - y_1 dx}{(x^2 + y_1^2)^{3/2}} + q_2 \frac{x dy_2 - y_2 dx}{(x^2 + y_2^2)^{3/2}} = 0$$

each part of which is homogeneous. Now put $y_1 = v_1 x$, $y_2 = v_2 x$ so that

$$x^2 dv = x dy - y dx$$

The result is then simply

$$q_1 \frac{dv_1}{(1 + v_1^2)^{3/2}} + q_2 \frac{dv_2}{(1 + v_2^2)^{3/2}} = 0$$

When this is integrated, we immediately obtain the equation of the lines of force due to the two charges:

$$q_1 \frac{v_1}{(1 + v_1^2)^{1/2}} + q_2 \frac{v_2}{(1 + v_2^2)^{1/2}} = \frac{q_1 y_1}{r_1} + \frac{q_2 y_2}{r_2} = \text{const.}$$

2.6. Note on Singular Solutions. Clairaut's Equation.—A first order equation of degree higher than the first may have a special kind of solution which is not obtainable by specifying the constants in its general solution. Thus consider

$$y = x \frac{dy}{dx} + \left(\frac{dy}{dx}\right)^2 \tag{2–10}$$

This equation may be solved by the following artifice. Differentiate once more, thus converting it into a second order equation, which, however, can easily be handled by the methods already discussed. The result is

$$\frac{dy}{dx} = \frac{dy}{dx} + x \frac{d^2y}{dx^2} + 2 \frac{dy}{dx} \frac{d^2y}{dx^2}$$

or

$$\left(x + 2 \frac{dy}{dx}\right) \frac{d^2y}{dx^2} = 0 \tag{2–11}$$

If now the first factor be cancelled, the equation is

$$\frac{d^2y}{dx^2} = 0$$

and has the solution $y = c_1 x + c_2$. This, however, is too general a result since it contains two constants of integration, a circumstance brought about by the arbitrary procedure of converting the original first order into a second order equation before solving. To satisfy eq. (10), it is necessary to substitute this solution and adjust c_2 in conformity with its demands. It is then seen that $c_2 = c_1^2$, and

$$y = cx + c^2$$

is the general solution of eq. (10).

But eq. (11) can also be satisfied by equating the first factor on the left to zero. This leads to

$$x + 2\frac{dy}{dx} = 0, \quad \text{or} \quad y = -\frac{x^2}{4} + c$$

This will satisfy eq. (10) if $c = 0$. Thus

$$y = -\frac{x^2}{4}$$

is another solution of the original differential equation, but one which is not derivable from its complete solution. It is called a *singular* solution. Inspection will show that it represents the *envelope* of all the straight lines which correspond to the complete solution. This is generally the meaning of singular solutions.

An equation of the form

$$y = x\frac{dy}{dx} + f\left(\frac{dy}{dx}\right)$$

is known to mathematicians as *Clairaut's equation.* Eq. (10) is a specimen of this type. Clairaut's equation can always be handled by the method here used and has the general solution

$$y = cx + f(c)$$

EQUATIONS OF HIGHER ORDER

A general method for solving certain differential equations of higher order will be presented in secs. 2.10–12. It seems appropriate, however, to discuss first a few special types of differential equations which can be solved by elementary means. While the theory given in this section is applicable to equations of any order, emphasis will be placed solely on second order equations because of their prominence in mathematical physics.

2.7. Linear Equations with Constant Coefficients; Right-Hand Member Zero.—In discussing this type of equation it becomes convenient to introduce a new notation; we write $D = d/dx$. A symbol such as D, which is meaningless unless applied to a function of x, and which is therefore not a mathematical quantity in the usual sense, bears the name "operator." In the present connection D may be regarded as nothing more than an abbreviation. Later, however, when the mathematics of quantum mechanics is to be studied, it will be found that operators such as D are entities of considerable significance which give rise to an operator algebra quite different in many respects from ordinary algebra. For the present we merely observe that a differential equation of the type under discussion in its most general form may be written:

$$D^n y + a_1 D^{n-1} y + a_2 D^{n-2} y + \cdots a_n y = 0 \qquad (2\text{–}12)$$

The a's are constants; the order of the equation is n. Consider now the differential equation

$$(D - r_1)(D - r_2) \cdots (D - r_n) y = 0 \qquad (2\text{–}13)$$

which must be understood to mean that the successive application of $d/dx - r_n$, $d/dx - r_{n-1}$, etc., upon y is to yield zero, the r's being constants. It is clear that (12) and (13) become identical when the r's are chosen to be the roots of the algebraic equation

$$r^n + a_1 r^{n-1} + a_2 r^{n-2} + \cdots + a_n = 0 \qquad (2\text{–}14)$$

Let us then attempt to solve (13). A particular solution of that equation is easily found, for if y satisfies

$$(D - r_n) y = 0$$

it will also satisfy (13), since further differentiations and multiplications by r will leave the right-hand side unchanged. But $(D - r_n)y = 0$ has the solution $y = c_n e^{r_n x}$, hence this is a particular solution of (13).

Furthermore, we observe that the order of the "factors" $(D - r_i)$ appearing in (13) is insignificant. Hence any factor may be written last, and this means that $c_{n-1} e^{r_{n-1} x}$ is also a particular solution, and so on. On adding all particular solutions, i.e., on putting

$$y = \sum_i c_i e^{r_i x} \qquad (2\text{–}15)$$

there results a solution with n independent arbitrary constants, and this must therefore be the complete solution. To summarize: in order to solve (12), first determine the roots of (13), which is known as the *auxiliary equation*. If these roots are denoted by r_i, the general solution is (15).

One point is to be noted. If the coefficients a appearing in (12) are functions of x, the decomposition into factors leading to (13) cannot be made by solving the auxiliary equation. The reason is that then the r's will also be functions of x, and

$$(D - r_1)(D - r_2) y \neq (D - r_2)(D - r_1) y$$

as the reader may easily verify. This state of affairs is expressed succinctly by saying that the operators $(D - r_1)$ and $(D - r_2)$ are *commutative* only if the r's are constants. For variable r's the order of the factors in (13) is also essential, so that the whole method of solution here discussed must fail.

Returning to the case of constant coefficients, one minor difficulty must be considered. Suppose that two roots of the auxiliary equation are equal. If they are called r_1 the supposedly general solution will contain the part $(c_1 + c_2)e^{r_1x}$ which is equivalent to ce^{r_1x}. One arbitrary constant has been lost and the solution obtained is no longer complete. To remove this fault we consider the two factors of (13) which gave rise to it and study the equation

$$(D - r_1)^2 y = 0 \tag{2–16}$$

One solution is certainly $y = e^{r_1x}$. Let us look for a general solution of the form $y = f(x)e^{r_1x}$. On substitution of this into (16) there results the following differential equation for $f(x)$:

$$\frac{d^2f}{dx^2} = 0$$

Hence $f = c_1x + c_2$, and the complete solution of (16) reads

$$y = (c_1x + c_2)e^{r_1x}$$

This shows that, when two roots of the auxiliary equation are equal and have the value r_1, the part of the solution $(c_1 + c_2)e^{r_1x}$ occurring in (15) must be replaced by $(c_1x + c_2)e^{r_1x}$. An extension of this argument leads to the general result: If r_i is a g-fold root of the auxiliary equation, the complete solution of (12) is

$$y = c_1e^{r_1x} + c_2e^{r_2x} + \cdots c_i(1 + a_1x + a_2x^2 + \cdots + a_{g-1}x^{g-1})e^{r_ix} + \cdots$$

Examples.

a. *Simple harmonic motion.*

When the force on a particle of mass m moving along the y-axis is equal to $-ky$, Newton's second law of motion reads:

$$m\frac{d^2y}{dt^2} = -ky$$

Here k, the force per unit of displacement of the particle, is known as the *stiffness* of the oscillator. If we denote the positive constant k/m by ω^2, the equation becomes $d^2y/dt^2 + \omega^2y = 0$. The roots of the auxiliary equation $r^2 + \omega^2 = 0$ are $r_1 = i\omega$, $r_2 = -i\omega$. Hence by (15)

$$y = c_1e^{i\omega t} + c_2e^{-i\omega t}$$

The constants c_1 and c_2 may of course be complex. This result may be written in two other, but equivalent, forms. On expanding the exponentials in sines and cosines we obtain

$$y = (c_1 + c_2) \cos \omega t + (c_1 - c_2)i \sin \omega t = C_1 \cos \omega t + C_2 \sin \omega t$$

This last result may also be stated as follows:

$$y = A \sin (\omega t + \delta) = A' \cos (\omega t + \delta')$$

where the new constants A, δ, and A', δ' are related to C_1 and C_2 by $A \sin \delta = C_1$, $A \cos \delta = C_2$; $A' \cos \delta' = C_1$, $-A' \sin \delta' = C_2$, or conversely $A^2 = A'^2 = C_1^2 + C_2^2$, $\delta = \tan^{-1} C_1/C_2$, $\delta' = \tan^{-1} C_2/C_1$.

b. *Chain sliding over a smooth peg.*

The chain (cf. Fig. 3) is sliding over the peg, the right end moving downward. Let the displacement of this end from 0, the point it would occupy in equilibrium, be y. If the linear density of the chain is λ, and its total length l, the mass to be accelerated is $l\lambda$. The resultant force is $2\lambda yg$. Hence, from Newton's second law,

$$l\lambda \frac{d^2y}{dt^2} = 2\lambda gy, \quad \text{or} \quad \frac{d^2y}{dt^2} - \frac{2g}{l} y = 0$$

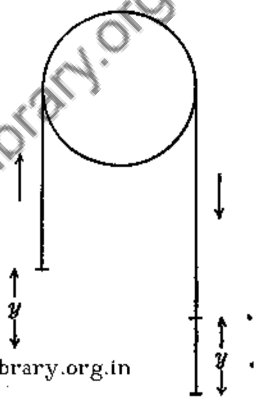

FIG. 2-3

The auxiliary equation has the roots $\pm\sqrt{2g/l}$, leading to the general solution $y = c_1e^{\sqrt{2g/l}\,t} + c_2e^{-\sqrt{2g/l}\,t}$. The constants may be fixed by supposing that, when $t = 0$, $y = y_0$ and $dy/dt = 0$. Then $c_1 + c_2 = y_0$; $c_1 - c_2 = 0$; and

$$y = \frac{y_0}{2} (e^{\sqrt{2g/l}\,t} + e^{-\sqrt{2g/l}\,t}) = y_0 \cosh \sqrt{\frac{2g}{l}}\, t$$

c. *Damped simple harmonic motion.*

When the motion of the oscillator considered in example (a) is damped, there is present, besides the restoring force $-ky$, a damping force proportional (at small velocities) to $-l(dy/dt)$, the negative sign indicating that the force *retards* the motion; l is known as the damping constant. The differential equation describing the motion is

$$\frac{d^2y}{dt^2} + 2b \frac{dy}{dt} + \omega^2 y = 0 \tag{2-17}$$

if b is written for the constant quantity $l/2m$. The auxiliary equation has the roots $-b \pm \sqrt{b^2 - \omega^2}$ so that the general solution becomes

$$y = c_1e^{(-b+\sqrt{b^2-\omega^2})t} + c_2e^{(-b-\sqrt{b^2-\omega^2})t}$$

To adjust the constants in conformity with physical conditions we suppose that, at $t = 0$, $y = y_0$ and $dy/dt = 0$. Then with the use of the abbreviation $R = \sqrt{b^2 - \omega^2}$

$$y = \frac{y_0}{2} e^{-bt}\left[\left(1 + \frac{b}{R}\right)e^{Rt} + \left(1 - \frac{b}{R}\right)e^{-Rt}\right] \tag{2-18}$$

Several special cases are of interest in this connection.

(α) $b > \omega$. R is then real, but smaller than b. Hence both terms of (18) represent an exponential decrease. The motion is not oscillatory.

(β) $b = \omega$. Then $R = 0$, and $y = y_0 e^{-bt}$. The motion is not oscillatory; it is said to be critically damped.

(γ) $b < \omega$. Then R is imaginary and may be written $R = i\omega'$, $\omega'^2 = \omega^2 - b^2$. Eq. (18) now reads

$$y = y_0 e^{-bt}\left(\cos \omega' t + \frac{b}{\omega'} \sin \omega' t\right)$$

or, in equivalent form,

$$y = \frac{\omega}{\omega'} y_0 e^{-bt} \sin (\omega' t + \delta)$$

where $\delta = \tan^{-1} \omega'/b$. This represents a damped sinusoidal motion of period $T = 2\pi/\sqrt{\omega^2 - b^2}$; the amplitude decreases exponentially as e^{-bt}.

d. *Natural oscillations in an electrical circuit.*

In a circuit containing R, L, and C, the sum of the "partial" electromotive forces due to inductance, resistance and capacitance equals the external e.m.f. If the latter is zero (natural oscillations) we have

$$L\frac{dI}{dt} + RI + \frac{q}{C} = 0$$

or, remembering that $I = dq/dt$,

$$\frac{d^2q}{dt^2} + \frac{R}{L}\frac{dq}{dt} + \frac{1}{LC}q = 0$$

This equation is of the form (17); the constants are $b = R/2L$, $\omega = (LC)^{-1/2}$. The solutions are already given in the foregoing example. In particular, if oscillations are to take place, $\omega > b$, i.e., $2\sqrt{L/C} > R$. In that case

$$q = \left(1 - \frac{R^2C}{4L}\right)^{-1/2} q_0 e^{-(R/2L)t} \sin\left(\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}\, t + \delta\right)$$

and

$$\delta = \tan^{-1}\sqrt{\frac{4L}{CR^2} - 1}$$

The initial conditions here are that at $t = 0$, the condenser has a charge q_0 and there is no current.

2.8. Linear Equations with Constant Coefficients; Right-Hand Member a Function of *x*.—We now restrict our considerations to differential equations of the second order. In terms of the notation of the foregoing section, the problem is to solve

$$(D^2 + a_1D + a_2)y = f(x) \tag{2-19}$$

If the roots of the auxiliary equation are r_1 and r_2, this equation takes the form

$$(D - r_1)(D - r_2)y = f(x) \tag{2-20}$$

Put $(D - r_2)y \equiv u$, so that $(D - r_1)u = f(x)$. This is a linear first order equation which can be solved by the method of sec. 3. It gives

$$u = e^{r_1x}\int e^{-r_1x}f(x)dx + c_1e^{r_1x} = e^{r_1x}(\varphi(x) + c_1)$$

if we define $\int_0^x e^{-r_1\xi}f(\xi)d\xi = \varphi(x)$. If this is substituted back into the definition of u, the result is $(D - r_2)y = e^{r_1x}(\varphi(x) + c_1)$, an equation which may again be treated in accordance with formula (6). Hence

$$y = e^{r_2x}\int e^{(r_1-r_2)x}[\varphi(x) + c_1]dx + c_2e^{r_2x}$$

$$= e^{r_2x}\int e^{(r_1-r_2)x}\varphi(x)dx + \frac{c_1}{r_1 - r_2}e^{r_1x} + c_2e^{r_2x}$$

On changing the meaning of the constant c_1, we write the solution of (19)

$$y = e^{r_2x}\int e^{(r_1-r_2)x}\varphi(x)dx + c_1e^{r_1x} + c_2e^{r_2x} \tag{2-21}$$

The form of this solution is interesting. The last two terms are identical with the solution of the homogeneous equation. They are called the *complementary function*, while the remainder, $e^{r_2x}\int e^{(r_1-r_2)x}\varphi(x)dx$, is known as the *particular integral*. Thus the "inhomogeneity" of the equation, $f(x)$, makes its appearance in the particular integral only. It is sometimes possible to find the particular integral of an equation like (19) by inspection, that is, by selecting any function which will satisfy the equation. When this is available one can make use of the fact just noted and form the complete solution by adding to this function the general solution of the homogeneous equation. Usually, however, the straightforward calculation of the particular integral is hardly more difficult.

The particular integral can be written in a form which is often more convenient in practice. On performing a partial integration we find

$$\int e^{(r_1-r_2)x}\varphi(x)dx = \frac{e^{(r_1-r_2)x}\varphi(x)}{r_1 - r_2} - \int \frac{e^{(r_1-r_2)x}}{r_1 - r_2}\frac{d\varphi}{dx}dx$$
$$= \frac{e^{(r_1-r_2)x}}{r_1 - r_2}\int e^{-r_1x}f(x)dx - \int \frac{e^{-r_2x}}{r_1 - r_2}f(x)dx$$

because $d\varphi/dx = e^{-r_1x}f(x)$. The particular integral then becomes

$$\frac{1}{r_1 - r_2}\left\{e^{r_1x}\int e^{-r_1x}f(x)dx - e^{r_2x}\int e^{-r_2x}f(x)dx\right\}$$

and finally

$$y = \frac{1}{r_1 - r_2}\left\{e^{r_1x}\int e^{-r_1x}f(x)dx - e^{r_2x}\int e^{-r_2x}f(x)dx\right\} + c_1e^{r_1x} + c_2e^{r_2x} \tag{2-22}$$

Examples.

a. *Forced oscillations of a mechanical or electrical system.* The equation to be considered is (17) but with a function of t instead of zero on the right. In most applications this function, which represents the impressed force divided by the mass of the oscillating system in the mechanical case, is a sinusoidal function of the time. Hence we are dealing with the differential equation

$$\frac{d^2y}{dt^2} + 2b\frac{dy}{dt} + \omega^2y = f_0 \sin \alpha t \tag{2-23}$$

As in sec. 7, example (c), the auxiliary equation has the roots

$$r_1 = -b + \sqrt{b^2 - \omega^2}, \quad r_2 = -b - \sqrt{b^2 - \omega^2}$$

If again we denote $\sqrt{b^2 - \omega^2}$ by R, the particular integral is

$$\text{P.I.} = \frac{e^{(-b+R)t}}{2R}\int e^{(b-R)t}f_0 \sin \alpha t dt - \frac{e^{-(b+R)t}}{2R}\int e^{(b+R)t}f_0 \sin \alpha t dt$$

The integrals here may be evaluated by means of the formulas on p. 43.

When this is done and the terms are suitably collected,

$$\text{P.I.} = \frac{f_0}{2R}\left\{\left[\frac{b-R}{(b-R)^2+\alpha^2} - \frac{b+R}{(b+R)^2+\alpha^2}\right]\sin\alpha t - \left[\frac{\alpha}{(b-R)^2+\alpha^2} - \frac{\alpha}{(b+R)^2+\alpha^2}\right]\cos\alpha t\right\}$$

$$= \frac{f_0}{(\omega^2-\alpha^2)^2+4\alpha^2 b^2}\left\{(\omega^2-\alpha^2)\sin\alpha t - 2b\alpha\cos\alpha t\right\}$$

To obtain the complete solution we must add to this the solution of (17). Hence

$$y = \frac{f_0}{(\omega^2-\alpha^2)^2+4\alpha^2 b^2}\left\{(\omega^2-\alpha^2)\sin\alpha t - 2b\alpha\cos\alpha t\right\} + e^{-bt}(c_1 e^{Rt} + c_2 e^{-Rt}) \quad (2\text{–}24)$$

It is seen that the complementary function decays exponentially with t and will be damped out eventually. It is therefore of little interest in physical applications. The amplitude of the oscillations,

$$\frac{f_0}{(\omega^2-\alpha^2)^2+4\alpha^2 b^2}$$

has a maximum when the impressed (angular) frequency has the value

$$\alpha = (\omega^2 - 2b^2)^{1/2}$$

This is said to be the condition of resonance between the impressed force and the vibrating system. If b is zero there occurs what is sometimes referred to as the "resonance catastrophe," for in that case the amplitude is infinite when $\alpha = \omega$.

(α) *Mechanical system.*

The present theory can be applied, for instance, to a mass m held in equilibrium by a spring of stiffness k and damping constant l. We then have, as in sec. 7c,

$$b = \frac{l}{2m}, \quad \omega^2 = \frac{k}{m}, \quad f_0 = \frac{F_0}{m}$$

Resonance occurs when

$$\alpha = \left(\frac{k}{m} - \frac{l^2}{2m^2}\right)^{1/2}$$

(β) *Electrical system.*

For an electrical system with an impressed electromotive force $E_0 \sin\alpha t$ we have (cf. sec. 7d), $b = R/2L$, $\omega = (LC)^{-1/2}$, $f_0 = E_0/L$. Resonance occurs when

$$\alpha = \left(\frac{1}{LC} - \frac{R^2}{2L^2}\right)^{1/2}$$

The solution (24) represents the charge, q, residing on the condenser at any instant. The current I is obtained by differentiating q with respect to the time. Both terms in braces then become positive, and

$$I = A[(\omega^2 - \alpha^2) \cos \alpha t + 2b\alpha \sin \alpha t]$$

where A stands for $E_0\alpha/L[(\omega^2 - \alpha^2)^2 + 4\alpha^2b^2]$. The power expended in the circuit is $\int_0^T EIdt$. This integral contains two terms, one with the integrand $\sin \alpha t \cos \alpha t$, the other with the integrand $\sin^2 \alpha t$. The first of these is 0 provided T is taken large enough to include a great number of cycles $2\pi/\alpha$, the last gives $\int_0^T \sin^2 \alpha t dt = T/2$. Hence the power expended is

$$Ab\alpha T$$

The part of the current proportional to $\cos \alpha t$ causes no power consumption; it is a " wattless " current which is always out of phase with the impressed electromotive force.

b. *Electrical polarization.*

An equation like (23) also describes the response of ordinary matter to an impinging electromagnetic wave. A light wave, for instance, which is polarized in such a way that its electric vector is along y, when incident upon an electron inside a refracting medium, will exert a force equal to $eE_0 \sin \alpha t$ upon this electron. Here E_0 is the amplitude of the electric vector of the light wave, e the charge on an electron, α the frequency of the light (assumed monochromatic). f_0 in (23) is then $(e/m)\, E_0$, m being the electron mass. The solution is given by (24). y represents the displacement of the electron under consideration at the time t. This gives rise to a dipole of moment ey. By " polarization " is meant the dipole moment per unit volume of the material, and this is obtained on multiplying the dipole moment due to one electron by the number of displaceable electrons per unit volume. If this number is N, then the polarization

$$P = \frac{Ne^2E_0}{m} \frac{\{(\omega^2 - \alpha^2) \sin \alpha t - 2b\alpha \cos \alpha t\}}{(\omega^2 - \alpha^2)^2 + 4\alpha^2b^2}$$

Further considerations of a physical nature[5] show how the index of refrac-

[5] See, for instance, Page, L., " Introduction to Theoretical Physics," D. Van Nostrand Co., p. 532 et seq.

tion and the conductivity of the substance may be deduced very easily from this expression for P.

2.9. Other Special Forms of Second Order Differential Equations.—a. An equation of the type

$$\frac{d^2y}{dx^2} = f(x) \tag{2-25}$$

can be integrated by the method of sec. 8. If this is done, only formula (21) is applicable, for the second formula (22) involves the quantity

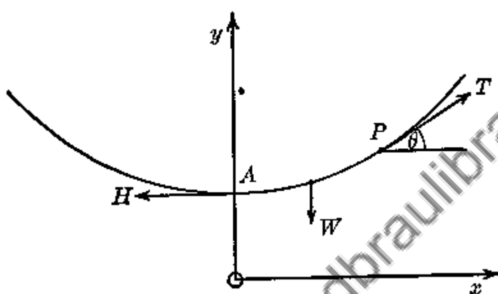

FIG. 2-4

$r_1 - r_2$, which is zero, the auxiliary equation corresponding to (23) having equal roots: $r_1 = r_2 = 0$. The solution is

$$y = \int \varphi(x)dx + c_1 + c_2x = \int \left[\int f(x)dx\right] + c_1 + c_2x$$

This procedure is here very artificial, of course, for this result could have been obtained directly by integrating (25) twice.

Example. *Suspension bridge.*

Consider the part of the cable between A and the variable point P. It is in equilibrium under the action of three forces: the horizontal force, H, the tension, T, at P, and the weight W of, or supported by, AP, which of course need not act at the middle of the segment. Hence we have

$$T \sin\theta = W; \quad T\cos\theta = H \quad \therefore \tan\theta = \left.\frac{dy}{dx}\right|_P = \frac{W}{H}$$

This relation is true for every point P, provided W is the load between A and P. It is generally more convenient to write the equation in terms of $w = dW/dx$, i.e., the load per unit horizontal distance; $w = w(x)$:

$$\frac{d^2y}{dx^2} = \frac{w(x)}{H} \tag{2-26}$$

In the case of the suspension bridge, the load is uniform along x, hence w = const.

Solution:

$$y = \frac{wx^2}{2H} + c_1x + c_2, \quad \text{a parabola}$$

b. *Equations not containing y.*

If the equation to be solved is

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

introduce the new variable $p = dy/dx$. The resulting equation

$$\frac{dp}{dx} = f(x,p)$$

can then be solved by one of the methods already discussed.

Example. *Cable hanging under its own weight.* The equation describing the cable is (26), but w is not constant. In this case it is dW/ds, the weight per unit length of cable, which is constant, provided the latter is uniform. Put $dW/ds = \lambda$. Then

$$\frac{d^2y}{dx^2} = \frac{\lambda}{H}\frac{ds}{dx} = \frac{\lambda}{H}\sqrt{1 + \left(\frac{dy}{dx}\right)^2}$$

From this $dp/\sqrt{1 + p^2} = (\lambda/H)dx$, so that

$$\sinh^{-1} p = \frac{\lambda}{H}x + c_1$$

If the origin is chosen at the lowest point of the cable, $c_1 = 0$, and

$$\frac{dy}{dx} = \sinh\frac{\lambda}{H}x; \quad y = \frac{H}{\lambda}\cosh\frac{\lambda}{H}x + c = \frac{H}{\lambda}\left(\cosh\frac{\lambda}{H}x - 1\right)$$

This curve is known as a catenary.

c. *Equations not containing x.*

$$\frac{d^2y}{dx^2} = f\left(y, \frac{dy}{dx}\right)$$

Again we put $dy/dx = p$, but now we write

$$\frac{d^2y}{dx^2} = \frac{dp}{dx} = \frac{dp}{dy}\cdot\frac{dy}{dx} = p\frac{dp}{dy}$$

The resulting equation

$$p\frac{dp}{dy} = f(y,p)$$

is solved for p, then integrated once more.

All linear homogeneous equations of the second order with constant coefficients discussed in sec. 2.7 can be solved by this method, but the treatment of sec. 2.7 is usually simpler.

Example. *Anharmonic oscillator.*

Differential equation:

$$\frac{d^2y}{dt^2} + \omega^2 y + \lambda y^2 = 0$$

Solution:

$$pdp = -(\omega^2 y + \lambda y^2)dy, \quad p = \frac{dy}{dt} = (c_1 - \omega^2 y^2 - \tfrac{2}{3}\lambda y^3)^{1/2}$$

The integration of this equation leads to an elliptic function.[6]

Problem. Solve the equation for the anharmonic oscillator by successive approximation, assuming that $\lambda y \ll \omega^2$.

Ans.

$$y = a\cos(\omega t + \epsilon) - \frac{\lambda a^2}{2\omega^2}[1 - \tfrac{1}{3}\cos 2(\omega t + \epsilon)]$$

INTEGRATION IN SERIES

A type of differential equation occurring very commonly in physics has the form

$$y'' + X_1 y' + X_2 y = 0 \tag{2-27}$$

where X_1 and X_2 are functions of x, the independent variable. Here and in the following, primes denote differentiations with respect to x. The methods developed in the preceding sections of this chapter are suitable for solving (27) when X_1 and X_2 have special forms, but are far from yielding solutions of that equation in general. In fact, such solutions are frequently not available in closed or finite form. For certain regions of x, however, they may be found in the form of convergent series by a procedure to be studied presently.

[6] See Peirce, B. O., "Short Table of Integrals." Introductory treatments of elliptic integrals may be found in "Higher Mathematics," by R. S. Burington and C. C. Torrance, McGraw-Hill Book Co., New York; "Higher Mathematics for Engineers and Physicists," by I. S. and E. S. Sokolnikoff, McGraw-Hill Book Co., New York.

2.10. Qualitative Considerations Regarding Eq. 27.—Before turning to the consideration of exact solutions of (27), a few remarks concerning their qualitative behavior in limited domains of x may be of value. To survey their behavior, it is often advisable to remove the first derivative occurring in (27), which is always possible by means of a simple transformation of the dependent variable. Instead of y, we introduce v, related to y by

$$y = ve^{-\frac{1}{2}\int X_1 dx}$$

When this is substituted into (27) and the exponential factor is then cancelled, there results an equation for v:

$$v'' + (X_2 - \tfrac{1}{2}X_1' - \tfrac{1}{4}X_1'^2)v = 0$$

from which the first derivative is absent. This represents essentially a relation between v and the curvature of v and may be written

$$v'' = f(x)v$$

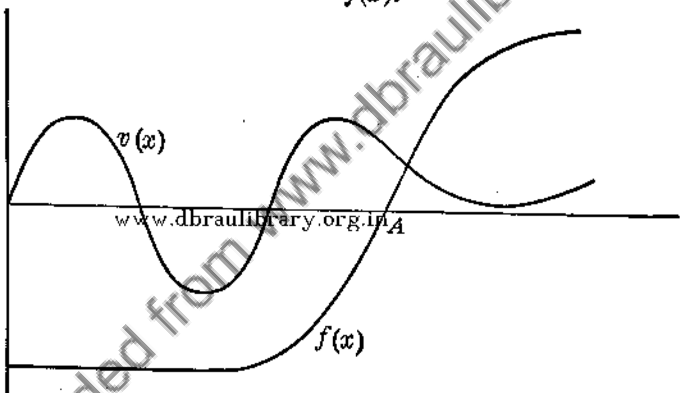

Fig. 2–5

One fact is at once apparent: provided v is finite, it has a point of inflexion wherever $f(x) = 0$. Furthermore, in regions where $f(x) > 0$ two facts are to be noted: If v is positive and has a positive slope, the slope will continually increase as x increases, causing v to grow rapidly; if v is positive and has a negative slope, the positive v'' will continually diminish its steepness, causing v to approach the x-axis and then in general to turn upwards again. For negative v the words "positive" and "negative" in the preceding sentence should be interchanged. This qualitative behavior is most easily remembered if we think of the special case in which $f(x) = \text{const.} = \omega^2 > 0$. The solution is then

$$v = c_1e^{\omega x} + c_2e^{-\omega x}$$

which typifies the foregoing remarks.

If, however, we consider a region in which $f(x) < 0$, the slope of positive v will be continually diminished. Thus if v starts out with positive slope this will soon be zero and then decrease until $v = 0$; as v then becomes negative its negative slope will increase until it is horizontal and v turns back toward zero. In short, v is oscillatory. This again is easily remembered if we consider the special case in which $f(x) = -\omega^2 < 0$ for it has the solution $v = c \sin (\omega x + \delta)$.

Fig. 5 illustrates these facts. To the left of A, v oscillates; at A it has a point of inflexion; to the right of A it is of exponential behavior.

2.11. Example of Integration in Series. Legendre's Equation.—To illustrate the method of series integration, let us postpone fundamental matters and start by studying a specific example. An equation of considerable interest is Legendre's; it has the form

$$(1 - x^2)y'' - 2xy' + l(l + 1)y = 0 \tag{2-28}$$

in which l is a constant. We attempt to find a solution which is a series in positive powers of x. If the lowest power occurring is κ, this solution will have the general form

$$y = \sum_{\lambda=1}^{\infty} a_\lambda x^{\kappa+\lambda} \tag{2-29}$$

Solving the differential equation then amounts to determining the coefficients a_λ. Whether the series converges can be tested after this has been achieved. At present it will be assumed that this is the case, and that (29) may be differentiated term by term. When (29) is substituted in (28) the result is

$$\sum_\lambda a_\lambda(\kappa + \lambda)(\kappa + \lambda - 1)x^{\kappa+\lambda-2} - \sum_\lambda a_\lambda[(\kappa + \lambda)(\kappa + \lambda - 1) + 2(\kappa + \lambda) - l(l + 1)]x^{\kappa+\lambda} = 0 \tag{2-30}$$

This equation must hold for every value of x, and this can be true only if the coefficient of *every* power of x is identically zero. Since λ cannot, by hypothesis, be negative, the lowest power of x occurring in (30) is $x^{\kappa-2}$, and it is present only in the first summation of (30). Thus we find, putting $\lambda = 0$ to obtain the term in question,

$$a_0\kappa(\kappa - 1) = 0 \tag{2-31}$$

a_0 is the lowest coefficient in our summation and hence not zero. Equation (31) therefore determines κ. It is often called the *indicial equation*. Clearly, two values of κ are permissible:

$$\kappa = 0, 1$$

Next, we see what further information eq. (30) will give. According to the foregoing, the coefficient of $x^{\kappa+j}$ must vanish for every positive integer j. Now the term corresponding to the $(\kappa+j)$-th power of x is obtained in the first summation by putting $\lambda = j+2$, in the second by putting $\lambda = j$. Hence

$$a_{j+2}(\kappa+j+2)(\kappa+j+1) = a_j[(\kappa+j)(\kappa+j+1) - l(l+1)]$$

or

$$a_{j+2} = \frac{(\kappa+j)(\kappa+j+1) - l(l+1)}{(\kappa+j+1)(\kappa+j+2)}\, a_j \tag{2-32}$$

Thus, if a_j is given, a_{j+2} can be computed from this relation. Starting with a_0, (32) permits us to obtain, successively, a_2, a_4, etc.; a_0, however, is arbitrary; it is one of the two arbitrary constants appearing in the general solution of a second order differential equation. On the other hand, if a_1 is assigned arbitrarily, all coefficients with odd subscripts are deducible from (32).

Choice 1. Let us take $\kappa = 0$. Eq. (32) then reads

$$a_{j+2} = \frac{j(j+1) - l(l+1)}{(j+1)(j+2)}\, a_j \tag{2-33}$$

On taking a_0 and a_1 as arbitrary constants, the solution becomes

$$y = \left(1 - \frac{l(l+1)}{2}x^2 - \frac{6 - l(l+1)}{12}\cdot\frac{l(l+1)}{2}x^4 + \cdots\right)a_0$$

$$+ \left(x + \frac{2 - l(l+1)}{6}x^3 + \frac{2 - l(l+1)}{6}\cdot\frac{12 - l(l+1)}{20}x^5 + \cdots\right)a_1$$

$$= \left(1 - \frac{l(l+1)}{2!}x^2 + \frac{l(l-2)(l+1)(l+3)}{4!}x^4 + \cdots\right.$$

$$+ (-1)^r\frac{l(l-2)\cdots(l-2r+2)(l+1)\cdots(l+2r-1)}{(2r)!}x^{2r}$$

$$\left.+ \cdots\right)a_0$$

$$+ \left(x - \frac{(l-1)(l+2)}{3!}x^3 + \frac{(l-1)(l-3)(l+2)(l+4)}{5!}x^5 + \cdots\right.$$

$$+ (-1)^r\frac{(l-1)(l-3)\cdots(l-2r+1)(l+2)\cdots(l+2r)}{(2r+1)!}x^{2r+1}$$

$$\left.+ \cdots\right)a_1 \tag{2-34'}$$

Choice 2. Let us take $\kappa = 1$. Eq. 5 then reads

$$a_{j+2} = \frac{(j+1)(j+2) - l(l+1)}{(j+2)(j+3)}\, a_j$$

If now we take again a_0 and a_1 as arbitrary constants, we find

$$y = x\left(1 + \frac{2 - l(l+1)}{6}x^2 + \frac{2 - l(l+1)}{6}\cdot\frac{12 - l(l+1)}{20}x^4 + \cdots\right)a_0$$
$$+ x\left(x + \frac{6 - l(l+1)}{12}x^3 + \frac{6 - l(l+1)}{12}\cdot\frac{20 - l(l+1)}{30}x^5 + \cdots\right)a_1$$
$$= x\left(1 - \frac{(l-1)(l+2)}{3!}x^2 + \frac{(l-1)(l-3)(l+2)(l+4)}{5!}x^4 + \cdots\right)a_0$$
$$+ x\left(x - \frac{(l-2)(l+3)}{12}x^3 + \frac{(l-2)(l-4)(l+3)(l+5)}{360}x^5 + \cdots\right)a_1 \qquad (2\text{-}35')$$

The terms multiplying a_0 in (35′) are seen to be identical with those multiplying a_1 in (34′); hence these two particular solutions are the same. The second part of (35′), however, does not agree with the first of (34′), both of which represent series in even powers of x. It might seem, therefore, as if we had obtained altogether *three* independent solutions, which is, of course, impossible. But closer inspection would show that the second part of (35′) is not a solution at all. This is seen at once if, after assuming any specific value for l, we substitute it back into the differential equation. The trouble is that, putting $\kappa = 1$ and $a_0 = 0$, we have carelessly discarded any constant term which might appear in the sequence. The present example indicates clearly that the solution of a differential equation is not an altogether mechanical matter and that caution must be used at every step. Summarizing, we observe that the significant parts of (34′) and (35′) are:

$$y = \left[1 - \frac{l(l+1)}{2!}x^2 + \frac{l(l-2)(l+1)(l+3)}{4!}x^4 + \cdots + (-1)^r \frac{l(l-2)\cdots(l-2r+2)(l+1)\cdots(l+2r-1)}{(2r)!}x^{2r} + \cdots\right]a_0 \qquad (2\text{-}34)$$

$$y = \left[x - \frac{(l-1)(l+2)}{3!}x^3 + \frac{(l-1)(l-3)(l+2)(l+4)}{5!}x^5 + \cdots + (-1)^r \frac{(l-1)(l-3)\cdots(l-2r+1)(l+2)\cdots(l+2r)}{(2r+1)!}x^{2r+1} + \cdots\right]a_1 \qquad (2\text{-}35)$$

Problem. Show that the equation $y'' + y = 0$, if integrated in series, has two particular solutions, one of which may be identified with the cosine series, the other with the sine series.

One further point should be observed. When any one term in (34) is zero, all succeeding terms vanish also and the series becomes a polynomial. The conditions under which infinite series like (34) reduce to polynomials are of great importance in many physical problems and will be discussed more fully later.

The work thus far has only established the fact that the series (34) and (35) are formal solutions of Legendre's equation, that is, they would satisfy (28) if substituted in it. Whether the solutions are of any interest depends on their convergence properties. A series converges if the ratio of the absolute values of two successive terms,

$$\frac{|u_{j+2}|}{|u_j|}$$

is smaller than unity for large j. Now this ratio is clearly

$$\frac{|a_{j+2}|}{|a_j|}x^2$$

But

$$\frac{|a_{j+2}|}{|a_j|}$$

is immediately obtainable from (33). As $j \to \infty$ it becomes 1. Hence the condition that (34) and (35) converge is that $x^2 < 1$, and this is true as long as $|x| < 1$. For values of x in the range $-1 < x < 1$ our solution is a significant one; for other values it fails. Is it possible to construct a solution valid for $|x^2| > 1$? This is indeed not difficult.

Let us suppose that y, instead of being given by (29), has the form $y = \sum_\lambda a_\lambda x^{\kappa-\lambda}$. Eq. (30) will then read

$$\sum_\lambda a_\lambda(\kappa - \lambda)(\kappa - \lambda - 1)x^{\kappa-\lambda-2}$$
$$-\sum_\lambda a_\lambda[(\kappa - \lambda)(\kappa - \lambda + 1) - l(l + 1)]x^{\kappa-\lambda} = 0$$

κ now denotes the *highest* power occurring in the series. The indicial equation is obtained by putting the coefficient of the highest power of x equal to zero. Thus

$$\kappa(\kappa + 1) - l(l + 1) = 0$$

whence

$$\kappa = l \quad \text{or} \quad -l - 1$$

As before, the coefficient of $x^{\kappa-j}$ must vanish for every positive integer j. This implies

$$a_{j-2}(\kappa - j + 2)(\kappa - j + 1) = a_j[(\kappa - j)(\kappa - j + 1) - l(l + 1)]$$

or, on replacing j by $j + 2$,

$$a_{j+2} = \frac{(\kappa - j)(\kappa - j - 1)}{(\kappa - j - 2)(\kappa - j - 1) - l(l+1)}\, a_j \qquad (2\text{-}36)$$

Choice 1. Let us take $\kappa = l$. Eq. (36) then reads

$$a_{j+2} = \frac{(l - j)(l - j - 1)}{(j + 2)(j - 2l + 1)}\, a_j$$

If a_0 is chosen arbitrarily, the series becomes

$$y = x^l \left(1 - \frac{l(l-1)}{2(2l-1)}\, x^{-2} + \frac{l(l-1)(l-2)(l-3)}{8(2l-1)(2l-3)}\, x^{-4} - \cdots \right.$$
$$\left. (-1)^r \frac{(l - 2r + 1)(l - 2r + 2) \cdots (l-1)l}{2r \cdots 2(2l - 2r + 1) \cdots (2l - 1)} x^{-2r} + \cdots \right) a_0 \qquad (2\text{-}37)$$

The series formally obtained by putting $a_0 = 0$ is of no interest since it violates the assumption, previously made, that κ, i.e., l, represents the highest power of the sequence. We shall therefore omit it at once.

Choice 2. Let us take $\kappa = -l - 1$. Then

$$a_{j+2} = \frac{(j + l + 1)(j + l + 2)}{(j + 2)(2l + j + 3)}\, a_j$$

If again we put $a_1 = 0$, there results the particular solution

$$y = x^{-l-1}\left(1 + \frac{(l+1)(l+2)}{2(2l+3)} x^{-2} + \frac{(l+1)(l+2)(l+3)(l+4)}{2 \cdot 4\,(2l+3)(2l+5)}\, x^{-4} + \cdots \right.$$
$$\left. + \frac{(l+1) \cdots (l+2r)}{2 \cdot 4 \cdots 2r(2l+3) \cdots (2l + 2r + 1)}\, x^{-2r} + \cdots \right) a_0 \qquad (2\text{-}38)$$

The two solutions (37) and (38) are independent, hence their sum represents the general solution of Legendre's equation. It is easily seen to converge if $|x| > 1$, *unless* l has such a value that the denominator of one of the coefficients in the series vanishes. This case will be studied shortly.

We are now in possession of two forms of solution of eq. (28). The first (eqs. 34 and 35) converges when $|x| < 1$, the second (eqs. 37 and 38) when $|x| > 1$. Under special circumstances, however, (34) or (35) as well as (37) or (38) may become polynomials, which remain finite for every finite value of x. It is interesting to see what happens to the various particular solutions when this contingency arises.

Eq. (34) reduces to a polynomial when l is an even positive or an odd negative integer (or zero).

a. Let l be even and positive; $l = 2k$. (34) then becomes

$$y = a\left(1 - \frac{l(l+1)}{2!}\, x^2 + \cdots (-1)^{l/2}\ \frac{l\,(l-2) \cdots 2(l+1) \cdots (2l-1)}{l!} x^l\right)$$

On the other hand, (37) becomes under these conditions

$$y = ax^l\left(1 - \frac{l(l-1)}{2(2l-1)}x^{-2} + \cdots \right.$$
$$\left. (-1)^{l/2}\frac{l!}{l(l-2)\cdots 2(l+1)\cdots(2l-1)}x^{-l}\right)$$

These two solutions become identical if the second is multiplied by the constant factor

$$(-1)^{l/2}\frac{l(l-2)\cdots 2(l+1)\cdots(2l-1)}{l!}$$

Hence the particular solution (34) coalesces with (37).

b. Let l be odd and negative. Inspection shows that (34) now becomes identical with (38).

Eq. (35) reduces to a polynomial when l is an odd positive or an even negative integer.

c. If l is odd and positive, (35) reads

$$y = a\left(x - \frac{(l-1)(l+2)}{3!}x^3 + \cdots \right.$$
$$\left. + (-1)^{(l-1)/2}\frac{(l-1)(l-3)\cdots 2(l+2)\cdots(2l-1)}{l!}x^l\right),$$

while (37) becomes

$$y = ax^l\left(1 - \frac{l(l-1)}{2(2l-1)}x^{-2} + \cdots \right.$$
$$\left. + (-1)^{(l-1)/2}\frac{l!}{2\cdot 4\cdots(l-1)(l+2)\cdots(2l-1)}x^{-l+1}\right)$$

These two expressions become identical when the second is multiplied by the coefficient of its last term in parenthesis.

d. If l is an even and negative integer (35) turns into (38).

Having established these important relations between solutions (34)–(38) we now return to the consideration of (37) and (38). Solutions (37) and (38) for integral values of l are of great importance in mathematical physics. If the constant a_0 in (37) is chosen to be

$$\frac{(2l)!}{2^l(l!)^2} = \frac{(2l-1)(2l-3)\cdots 1}{l!}$$

the resulting polynomial of degree l is called a *Legendre polynomial* (or Legendre coefficient or " zonal harmonic "). It is usually denoted by P_l.

For purposes of reference we write it down again:

$$P_l(x) = \frac{1 \cdot 3 \cdot 5 \cdots (2l-1)}{l!} \left\{ x^l - \frac{l(l-1)}{2(2l-1)} x^{l-2} + \frac{l(l-1)(l-2)(l-3)}{2 \cdot 4(2l-1)(2l-3)} x^{l-4} - \cdots \right\} \quad (2\text{-}39)$$

The series here is to be continued down to the constant term. On the other hand, (38) with the constant a_0 chosen to be $2^l(l!)^2/(2l+1)!$, l being a positive integer, is often denoted by Q_l. It is an infinite series:

$$Q_l = \frac{l!}{1 \cdot 3 \cdots (2l+1)} \left\{ x^{-l-1} + \frac{(l+1)(l+2)}{2(2l+3)} x^{-l-3} + \cdots + \frac{(l+1)\cdots(l+2r)}{2 \cdot 4 \cdots 2r(2l+3)\cdots(2l+2r+1)} x^{-l-2r-1} + \cdots \right\} \quad (2\text{-}40)$$

The following facts will be noted:

When l is a positive integer, (37) is a polynomial, but (38) is an infinite series. The general solution of (28) is a linear combination of (37) and (38).

When l is a negative integer, (37) is an infinite series, and (38) is a polynomial. The general solution of (28) is a linear combination of (37) and (38).

When $2l$ is equal to some *positive odd* integer, solution (37) degenerates into (38). To see this, suppose $2l = 2n - 1$. There will then appear a vanishing denominator in the coefficient of x^{l-2n} and in every subsequent term of (37). To remove these infinities one may multiply the entire series by $(n - r)$, which causes all terms of order higher than $l - 2n$ to vanish while the others remain finite. Hence the series begins with the power $x^{l-2n} = x^{-l-1}$, and inspection shows it then to be identical with (38). In this case, our method has yielded but *one* particular solution, and this is an infinite series. Procedures leading to a general solution are discussed in treatises on Differential Equations.[7]

When $2l$ is equal to an *odd negative* integer, (38) degenerates into (37) in a manner similar to the above. In that case also no general solution can be obtained by the present method.

Having now given a fairly complete mathematical analysis of the solutions of Legendre's equation, we state some conclusions of practical importance. In almost all applications (cf. Chapters 7, 8, 11) the independent variable x appearing in eq. (28) is the cosine of an angle. *The functions of interest are therefore those which remain finite for all values which $x = \cos\theta$ can assume;* these values include $x = \pm 1$. Such functions exist only when

[7] See Forsyth, A. R., "Differential Equations," Macmillan Co., London, 1914.

l is a positive or a negative integer, as we have shown. But when l is an integer, consideration may be limited to solutions (37) and (38), because the others reduce to these. Moreover, inspection shows that solution (38) with l replaced by $-(l+1)$ is the same as solution (37). Hence we may further limit our consideration to positive values of l (including 0) and retain only (37) as a significant solution. Finally we note that (37) is identical with (39). Hence:

In physio-chemical problems, where $x = \cos\theta$, the only solution of Legendre's equation which is of practical interest is $P_l(\cos\theta)$.

Problems.

a. Prove that, when l is an even negative integer, the expressions (35) and (38) become identical.

b. Prove that, when $2l$ is an odd negative integer, expressions (37) and (38) become identical.

Differential Equation for Associated Legendre Functions, or Associated Spherical Harmonics.

An equation similar to Legendre's plays a considerable rôle in mathematical physics. It is[8]

$$(1-x^2)y'' - 2xy' + \left[l(l+1) - \frac{m^2}{1-x^2}\right]y = 0 \qquad (2\text{-}41)$$

where l and m are both integers, and has a particular solution:

$$y = (1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x) \qquad (2\text{-}42)$$

The other particular solution is related to Q_n and is rarely of interest in applications. To construct (42) by the method of series integration is perfectly feasible, but we shall here use a simpler method based on the foregoing results. If $P_l(x)$ is a solution of

$$(1-x^2)y'' - 2xy' + l(l+1)y = 0$$

then

$$\frac{d^m}{dx^m}P_l(x)$$

[8] The equation occurs more commonly in the equivalent forms

$$\frac{d^2y}{d\theta^2} + \cot\theta\frac{dy}{d\theta} + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]y = 0$$

or

$$\frac{1}{\sin\theta}\left[\frac{d}{d\theta}\left(\sin\theta\frac{dy}{d\theta}\right)\right] + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]y = 0$$

which reduce to (41) on substitution of $\cos\theta = x$.

for which we shall write $P_l^{(m)}(x)$, satisfies the equation

$$(1 - x^2)P_l^{(m)''} - 2(m+1)xP_l^{(m)'} + [l(l+1) - m(m+1)]P_l^{(m)} = 0 \tag{2–43}$$

as is seen when Legendre's equation is differentiated m times. Now let

$$P_l^{(m)}(x) = (1 - x^2)^r y \tag{2–44}$$

and determine, by substituting this into (43), what differential equation y will satisfy. After substitution, (43) will read

$$\begin{aligned}(1 - x^2)^{r-1}\{ &(4r^2x^2 - 2r - 2rx^2)y - 4r(1 - x^2)xy' + (1 - x^2)^2y'' \\ &- 2(m+1)(1 - x^2)xy' + 4r(m+1)x^2y + [l(l+1) \\ &- m(m+1)](1 - x^2)y\} = 0\end{aligned} \tag{2–44}$$

If here the special value $r = -m/2$ is chosen, this equation reduces to (41). We have shown, therefore, that (44) is true with $r = -m/2$ and hence that

$$y = (1 - x^2)^{m/2}P_l^{(m)}(x)$$

as was asserted. The function $P_l^{(m)}$, which is a polynomial of degree $l - m$ and which satisfies eq. (43), is sometimes referred to by physicists as *Helmholtz' function*. The function (42) is known as an associated Legendre function, or more frequently, an *associated spherical harmonic*.

2.12. General Considerations Regarding Series Integration. Fuchs' Theorem.—Before continuing, the reader will wish to know the limits of applicability of the method applied in sec. 2.11, and in particular what properties of the solution one may read directly from the differential equation. First, then, let us ask the question: Will the method described in sec. 2.11 always work? In preparation for the answer, we consider the differential equation

$$y'' + y/x^3 = 0$$

On putting $y = \sum a_\lambda x^{\kappa+\lambda}$ it is seen that

$$\sum_\lambda a_\lambda(\kappa + \lambda)(\kappa + \lambda - 1)x^{\kappa+\lambda-2} = -\sum_\lambda a_\lambda x^{\kappa+\lambda-3}$$

The indicial equation, obtained by putting the coefficient of the lowest power of x equal to zero, simply reads

$$a_0 = 0$$

and does not determine κ. Furthermore,

$$a_{j+1} = -(\kappa + j)(\kappa + j - 1)a_j$$

so that $a_1 = -a_0(\kappa - 1)\kappa$. Since $a_0 = 0$, this means that either $\kappa = \infty$ or a_1 is also zero. In neither case do we get any solution at all.

Equally instructive is the equation

$$y'' + \frac{y'}{x^2} = 0$$

Its indicial equation yields $\kappa = 0$. The recurrence relation between coefficients is

$$a_{j+1} = -\frac{j(j-1)}{j+1} a_j$$

Thus we have apparently determined a solution. But let us apply a convergence test. Denoting again the terms of the series by u_r one sees that

$$\lim_{n\to\infty} \frac{|u_{n+1}|}{|u_n|} = \lim_{n\to\infty} \frac{|a_{n+1}|x^{n+1}}{|a_n|x^n} = \lim_{n\to\infty} \frac{(n-1)n}{n+1} \cdot x = nx$$

This is greater than 1 as $n \to \infty$ for every finite value of x, so that there is no range of x at all in which the series converges. Again, the method fails.

To enlarge our outlook, let us now return to the general form of the equation we wish to solve, that is, to eq. (27). As a rule there will be values of x for which one or both of the functions X_1 and X_2 become infinite. If $x = x_0$ is such a value, then x_0 is said to be a *singular point* of the equation. It is at such singular points that the method of integration in series may break down. To be more specific, a solution of the form $y = \sum_\lambda a_\lambda (x - x_0)^{\kappa+\lambda}$ may not exist at singular points x_0.

In dealing with Legendre's equation, a power series development was attempted about the point $x_0 = 0$. It succeeded because, after writing the equation in the form (27), neither $X_1 = -2x/(1 - x^2)$ nor $X_2 = l(l + 1)/(1 - x^2)$ becomes infinite at $x = 0$. But the points $x = \pm 1$ are singular points of the equation, and it is for this reason that the general solution obtained breaks down at these two points. Again, the two equations just considered, $y'' + x^{-3}y = 0$ and $y'' + x^{-2}y' = 0$ possess a singular point at $x = 0$, and this is the cause of the failure of the present method.

But while the method *often* fails if the differential equation has a singular point at the place where the power series development is attempted, it does not always do so. For instance, the equation

$$y'' + x^{-1}y' - x^{-2}y = 0$$

may be developed in the form $y = \sum_\lambda a_\lambda x^{\kappa+\lambda}$ despite its singularities at $x = 0$. The indicial equation yields $\kappa = \pm 1$. When the positive sign is chosen, the coefficients must satisfy the equation

$$[(j + 1)^2 - 1]a_j = 0$$

which is no longer a recurrence relation but serves to determine the coefficients just as well. For it says that every $a_j = 0$, except for $j = 0$.

The corresponding solution is $y = a_0 x$. For $\kappa = -1$ we have

$$[(j-1)^2 - 1]a_j = 0$$

and this indicates that all coefficients must be zero except that corresponding to $j = 0$ and to $j = 2$. Hence the solution is

$$y = x^{-1}(a_0 + a_2 x^2)$$

The constants a_0 and a_2 are arbitrary, which implies that the solution is a general one, including $y =$ const. x as a special case. Obviously, then, it is important to settle what kind of singularities do, and what kind do not, permit an integration in series about the singular point.

This issue is settled by an important theorem due to Fuchs, which states the following:

If the differential equation

$$y'' + X_1 y' + X_2 y = 0$$

possesses a singular point at $x = x_0$, then a convergent development of the solution in a power series about the point $x = x_0$ having only a finite number of terms with negative exponents is nevertheless possible provided that $(x - x_0)X_1(x_0)$ and $(x - x_0)^2 X_2(x_0)$ remain finite.

This clearly is true for the equation

$$y'' + x^{-1}y' - x^{-2}y = 0$$

at $x_0 = 0$, but not for

$$y'' + x^{-2}y' = 0$$

Thus the results just obtained are accounted for. The proof of Fuchs' theorem is a matter of some length and will not be undertaken here.[9] In conformity with the theorem singularities in X_1 and X_2 occurring at $x = x_i$ which are removable by multiplication by the factors $(x - x_i)$ and $(x - x_i)^2$ respectively are called *non-essential* singularities of the differential equation; all others are essential ones.[10] All regular and non-essentially singular points are sometimes referred to as regular points of the differential equations (German: "Stellen der Bestimmtheit"). An equation which has no essential singularities in the entire infinite complex plane is said to belong to the Fuchsian class of differential equations.

[9] See, for instance, Schmidt, H., "Theorie der Wellengleichung," Leipzig, 1931.

[10] Whether the point at infinity is an essentially singular one cannot at once be seen in this way. To examine it the transformation $\xi = 1/x$ must be made. One may then show that the point at infinity is *essentially singular* if $X_1 x$ or $X_2 x^2$ become infinite there; it is *non-essentially singular* if $2x - X_1 x^2 \to \infty$ or $X_2 x^4 \to \infty$; otherwise it is regular.

A final remark on the nature of the solutions obtained by the method of integration in series is in order. Even if the point at which the development is made satisfies the Fuchs conditions it may not be possible to obtain *two independent* solutions which, when combined linearly with the use of two arbitrary constants, will yield the general solution. If this process is to produce a general solution, further conditions must be met. Since general solutions are not often required in physical and chemical applications, this matter will not be considered in detail here.[11] We note, however, that two independent solutions in the form $y_1 = \sum a_\lambda (x - x_0)^{\kappa_1+\lambda}$ and $y_2 = \sum a_\lambda (x - x_0)^{\kappa_2+\lambda}$ can always be obtained when the two roots of the indicial equation, κ_1 and κ_2, do not differ by an integer or by zero.

SPECIAL EQUATIONS SOLVABLE BY SERIES INTEGRATION

2.13. Gauss' (Hypergeometric) Differential Equation.—

$$(x^2 - x)y'' + [(1 + \alpha + \beta)x - \gamma]y' + \alpha\beta y = 0 \qquad (2\text{–}45)$$

The parameters α, β, γ are constants, and it will be assumed that γ is not an integer. Eq. (45) has singularities at 0, 1, and ∞, but they are all nonessential. On development about $x = 0$, the indicial equation reads

$$\kappa(\kappa - 1) + \kappa\gamma = 0$$

hence $\kappa = 0, 1 - \gamma$. Choosing $\kappa = 0$, we obtain the recurrence formula

$$a_{j+1} = \frac{(\alpha + j)(\beta + j)}{(j + 1)(j + \gamma)} a_j \qquad (2\text{–}46)$$

and hence the particular solution

$$y = a\left\{1 + \frac{\alpha\beta}{1\cdot\gamma}x + \frac{\alpha(\alpha+1)\,\beta(\beta+1)}{1\cdot 2\cdot\gamma(\gamma+1)}x^2 + \cdots + \frac{\alpha(\alpha+1)\cdots(\alpha+r-1)\cdot\beta(\beta+1)\cdots(\beta+r-1)}{r!\,\gamma(\gamma+1)\cdots(\gamma+r-1)}x^r + \cdots\right\} \qquad (2\text{–}47)$$

The series in {} is known as the *hypergeometric series.* It converges if $|x| < 1$. For $\alpha = 1$, $\beta = \gamma$ it reduces to the ordinary geometric series; hence its name. It is customary to denote the hypergeometric series by $F(\alpha,\beta,\gamma;x)$. With this abbreviation, then, this particular solution is

$$y = aF(\alpha,\beta,\gamma;x)$$

Next, we take $\kappa = 1 - \gamma$. The recurrence relation reads

$$a_{j+1} = \frac{(\alpha - \gamma + j + 1)(\beta - \gamma + j + 1)}{(j + 1)(j + 2 - \gamma)} a_j \qquad (2\text{–}48)$$

[11] For particulars, see Bôcher, M., "Regular Points of Linear Differential Equations of the Second Order," Harvard University Press.

When the new constants: $\alpha' = \alpha - \gamma + 1, \beta' = \beta - \gamma + 1, \gamma' = 2 - \gamma$, are introduced in (48) it becomes

$$a_{j+1} = \frac{(\alpha' + j)(\beta' + j)}{(j + 1)(j + \gamma')} a_j$$

that is, it takes the same form as (46). The particular solution corresponding to (48) may therefore be written

$$ax^{1-\gamma}F(\alpha - \gamma + 1, \beta - \gamma + 1, 2 - \gamma; x)$$

We have thus arrived at the following general solution of (45):

$$y = AF(\alpha,\beta,\gamma;x) + Bx^{1-\gamma}F(\alpha - \gamma + 1, \beta - \gamma + 1, 2 - \gamma; x) \quad (2\text{-}49)$$

whose range of convergence is $|x| < 1$.

There is an interesting and sometimes useful relation between the solutions of Gauss' and those of Legendre's equation. Let us introduce in (45) the new independent variable ξ, given by

$$x = \tfrac{1}{2}(1 - \xi)$$

so that it takes the form

$$(1 - \xi^2)\frac{d^2y}{d\xi^2} + [1 + \alpha + \beta - 2\gamma - (\alpha + \beta + 1)\xi]\frac{dy}{d\xi} - \alpha\beta y = 0 \quad (2\text{-}50)$$

This reduces to Legendre's equation (28) if we specify the constants to be

$$\alpha = l + 1, \quad \beta = -l, \quad \gamma = 1$$

One particular solution of Legendre's equation is therefore

$$y = aF\left(l + 1, -l, 1; \frac{1 - \xi}{2}\right)$$

From the fact that this solution, expanded in powers of ξ, starts with a constant term it is clear that it must be identical (aside from a constant factor) with (34). In particular, if l is a positive integer, it must be P_l. This happens to be true, as the reader may verify, even with respect to the constant factor if P_l is defined as in (39). Thus

$$P_l(\xi) = F\left(l + 1, -l, 1; \frac{1 - \xi}{2}\right) \quad (2\text{-}51)$$

An equation known to mathematicians as *Tschebyscheff's* results when in (50) we specialize the constants as follows:

$$\alpha = -\beta = n, \quad \text{an integer}; \quad \gamma = \tfrac{1}{2}$$

The equation then reads:

$$(1 - \xi^2)\frac{d^2y}{d\xi^2} - \xi\frac{dy}{d\xi} + n^2y = 0 \quad (2\text{-}52)$$

Its solution is clearly

$$y(\xi) = AF\left(n, -n, \tfrac{1}{2}; \frac{1-\xi}{2}\right) + B\left(\frac{1-\xi}{2}\right)^{1/2} F\left(n+\tfrac{1}{2}, -n+\tfrac{1}{2}, \tfrac{3}{2}; \frac{1-\xi}{2}\right) \tag{2-53}$$

The first particular solution here written is a polynomial known as the *Tschebyscheff polynomial*, of degree n. If multiplied by the proper factor it has the alternative form:

$$T_n(x) = 2^{n-1}\left(x^n - \frac{n}{1!\,2^2}x^{n-2} + \frac{n(n-3)}{2!\,2^4}x^{n-4} - \frac{n(n-4)(n-5)}{3!\,2^6}x^{n-6} + \cdots\right) \tag{2-54}$$

The function $F(\alpha,\beta,\gamma;x)$ reduces to a polynomial when $\alpha = -n$, n being a positive integer, as may be seen from its definition (47). The resulting polynomial, which is of degree n, is known as a *Jacobi polynomial*, defined as follows:

$$J_n(p,q;x) \equiv F(-n, p+n, q; x) \tag{2-55}$$

It satisfies the differential equation

$$(x^2 - x)y'' + [(1+p)x - q]y' - n(p+n)y = 0 \tag{2-56}$$

in which q must satisfy $q > 0$. Substitution of $\alpha = -n$, $\beta = p + n$, $\gamma = q$ into (47) shows that[12]

$$J_n(p,q;x) = 1 + \sum_{\lambda=1}^{n} (-1)^\lambda \binom{n}{\lambda} \frac{(p+n)(p+n+1)\cdots(p+n+\lambda-1)}{q(q+1)\cdots(q+\lambda-1)} x^\lambda$$

Problem. Find the solution of (45) about the point $x = 1$; i.e., find solutions of the form

$$y = \sum_\lambda a_\lambda (x-1)^{\kappa+\lambda}$$

Ans.

$$y = AF(\alpha,\beta,\alpha+\beta-\gamma+1; 1-x) + B(1-x)^{\gamma-\alpha-\beta}F(\gamma-\beta, \gamma-\alpha, 1-\alpha-\beta+\gamma; 1-x)$$

2.14. Bessel's Equation.—

$$x^2y'' + xy' + (x^2 - n^2)y = 0 \tag{2-57}$$

n is a constant. Since the equation is regular at $x = 0$, its solution may be developed as a power series about that point. The indicial equation

$$(\kappa^2 - n^2)a_0 = 0$$

[12] Cf. eq. 12–2 for the definition of $\binom{n}{\lambda}$.

has the two roots $\kappa = \pm n$. According to the remarks at the end of sec. 2.12 we can obtain two independent particular solutions if $2n$ is not an integer; if it is, the method may allow us to determine only one. Taking $\kappa = n$ one finds

$$y = a_0 x^n \left\{1 - \frac{x^2}{2(2n+2)} + \frac{x^4}{2 \cdot 4(2n+2)(2n+4)} - \cdots + (-1)^r \frac{x^{2r}}{2 \cdot 4 \cdots 2r(2n+2)(2n+4)\cdots(2n+2r)} + \cdots\right\} \tag{2-58}$$

For $\kappa = -n$

$$y = a_0 x^{-n} \left\{1 + \frac{x^2}{2(2n-2)} + \frac{x^4}{2 \cdot 4(2n-2)(2n-4)} + \cdots + \frac{x^{2r}}{2 \cdot 4 \cdots 2r(2n-2)(2n-4)\cdots(2n-2r)} + \cdots\right\} \tag{2-59}$$

When the constant a_0 in (58) is chosen to be[13] $1/[2^n\Gamma(n+1)]$, the resulting expression

$$y = J_n(x) \equiv \sum_{\lambda=0}^{\infty} \frac{(-1)^\lambda}{\Gamma(\lambda+1)\Gamma(\lambda+n+1)} \left(\frac{x}{2}\right)^{n+2\lambda} \tag{2-60}$$

is called a *Bessel function* of order n.

When (59) is multiplied by the same factor it becomes $J_{-n}(x)$. Hence the complete solution of Bessel's equation (when n is not an integer) is

$$y = AJ_n(x) + BJ_{-n}(x) \tag{2-61}$$

Inspection of (58) and (59) shows that no difficulty arises when n is half-integral, although the difference of the roots of the indicial equation is an integer. But if n is an integer, J_{-n} is no longer independent of J_n. For in that case the coefficient of x^{2n} in (59) has a vanishing term in the denominator, and every subsequent coefficient likewise becomes infinite. Multiplication by the vanishing term makes every term preceding the n-th zero. The series then starts with x^n and is seen to be identical (except for a constant multiplier) with (58). For integral n, therefore, we have obtained only one solution, namely $J_n(x)$.[14] By choosing the constants A and B of

[13] The Gamma function appearing here is a generalization of the factorial $n!$ which is defined only for integers (and zero). If n is an integer, $\Gamma(n+1) = n!$. In general, $\Gamma(x) = \int_0^\infty e^{-t}t^{x-1}dt$; it is easily seen to reduce to $n!$ when $x = n$. Moreover, this integral defines the "smoothest" function which takes on the values $n!$ at the integers. Cf. sec. 3.2.

[14] The second particular solution for integral n is derived in Forsyth, "Differential Equations," Macmillan, p. 182.

(61) suitably, several particular solutions of Bessel's equation (such as Neumann's and Hankel's functions) having useful properties may be constructed. They will be discussed in sec. 3.9.

2.15. Hermite's Differential Equation.—

$$y'' - 2xy' + 2\alpha y = 0; \quad \alpha = \text{constant} \tag{2-62}$$

The roots of the indicial equation are $\kappa = 0, 1$; the recurrence relations between the coefficients

$$a_{j+2} = \frac{2(\kappa + j) - 2\alpha}{(\kappa + j + 2)(\kappa + j + 1)} a_j$$

For $\kappa = 0$ we find the solution

$$y = a_0 \left(1 - \frac{2\alpha}{2!} x^2 + \frac{2^2\alpha(\alpha - 2)}{4!} x^4 - \frac{2^3\alpha(\alpha - 2)(\alpha - 4)}{6!} x^6 + \cdots + (-2)^r \frac{\alpha(\alpha - 2) \cdots (\alpha - 2r + 2)}{(2r)!} x^{2r} + \cdots \right) \tag{2-63}$$

while for $\kappa = 1$

$$y = a_0 x \left(1 - \frac{2(\alpha - 1)}{3!} x^2 + \frac{2^2(\alpha - 1)(\alpha - 3)}{5!} x^4 - \cdots + (-2)^r \frac{(\alpha - 1)(\alpha - 3) \cdots (\alpha - 2r + 1)}{(2r + 1)!} x^{2r} + \cdots \right) \tag{2-64}$$

The general solution of Hermite's equation is a superposition of these. If α is an even integer n, (63) reduces to an even polynomial of degree n. On choosing for a_0 the value

$$(-1)^{n/2} \frac{n!}{\left(\frac{n}{2}\right)!}$$

this polynomial becomes

$$H_n(x) = (2x)^n - \frac{n(n-1)}{1!} (2x)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!} (2x)^{n-4} - \cdots \tag{2-65}$$

and this is known as the *Hermite polynomial* of degree n. If α is an odd integer, n, (64) reduces to an odd polynomial of degree n. In fact if we choose for a_0 the value

$$(-1)^{(n-1)/2} \frac{2 \cdot n!}{\left(\frac{n-1}{2}\right)!}$$

that particular solution also takes on the form $H_n(x)$.

An equation very similar to that of Hermite is

$$y'' + (1 - x^2 + 2\alpha)y = 0 \qquad (2\text{–}66)$$

For if we put $y = e^{-x^2/2}v$, so that $y'' = \{(x^2 - 1)v - 2xv' + v''\}e^{-x^2/2}$, the equation turns into

$$v'' - 2xv' + 2\alpha v = 0$$

which is identical with (62). Hence the solution of (66) is simply any solution of Hermite's equation, multiplied by $e^{-x^2/2}$.

2.16. Laguerre's Differential Equation.—

$$xy'' + (1 - x)y' + \alpha y = 0; \quad \alpha = \text{constant} \qquad (2\text{–}67)$$

has a non-essential singularity at the origin. Developing about $x = 0$, the indicial equation has the single root $\kappa = 0$. Only one solution will be obtained, this being of considerable importance in physics. The recurrence relation reads:

$$a_{j+1} = \frac{j - \alpha}{(j + 1)^2} a_j$$

hence

$$y = a_0\left(1 - \alpha x + \frac{\alpha(\alpha - 1)}{(2\,!)^2} x^2 - \cdots + (-1)^r \frac{\alpha(\alpha - 1) \cdots (\alpha - r + 1)}{(r\,!)^2} x^r + \cdots\right) \qquad (2\text{–}68)$$

This expression becomes a polynomial when $\alpha = n$, a positive integer. On putting

$$a_0 = (-1)^n n\,!$$

and for integral n, y becomes the *Laguerre polynomial* of degree n:

$$L_n(x) = (-1)^n \left(x^n - \frac{n^2}{1\,!} x^{n-1} + \frac{n^2(n - 1)^2}{2\,!} x^{n-2} + \cdots + (-1)^n n\,!\right) \qquad (2\text{–}69)$$

A differential equation at once reducible to Laguerre's is

$$xy'' + (k + 1 - x)y' + (\alpha - k)y = 0, \quad k \text{ an integer} \geq 0 \qquad (2\text{–}70)$$

It results when (67) is differentiated k times and y is replaced by its k-th derivative. Hence a solution of (70) for integral and positive α and k is

$$y = \frac{d^k}{dx^k} L_n(x) \equiv L_n^k(x)$$

This is sometimes called the *associated Laguerre polynomial* of degree $n - k$.

A third function closely related to the Laguerre polynomials satisfies the differential equation

$$xy'' + 2y' + \left[n - \frac{k-1}{2} - \frac{x}{4} - \frac{k^2 - 1}{4x}\right] y = 0 \qquad (2\text{–}71)$$

If we substitute in this equation $y = e^{-x/2}x^{(k-1)/2}v$, then v is seen to be a solution of

$$xv'' + (k + 1 - x)v' + (n - k)v = 0$$

Comparison with (70) shows, therefore, that $v = L_n^k(x)$. Hence a particular solution of (71) is

$$y = e^{-x/2}x^{(k-1)/2}L_n^k(x) \qquad (2\text{–}72)$$

This function is known as an *associated Laguerre function;* it is of great importance in the theory of the hydrogen atom. We observe that if n in (71) were not an integer but any constant α, the corresponding solution of (71) would be

$$y = e^{-x/2}x^{(k-1)/2} \frac{d^k}{dx^k} L_\alpha(x)$$

where L_α is written for the series (68); provided, of course, that k is a positive integer. This solution would no longer be a polynomial in x multiplied by $e^{-x/2}$, but an infinite sequence.

2.17. Mathieu's Equation.—In the previous sections attention has been given to differential equations in which X_1 and X_2[15] were algebraic functions of x. Equations sometimes arise in which these functions are periodic. The simplest instance of these is *Mathieu's equation*, usually written in the form

$$\frac{d^2y}{dx^2} + (a + 16b \cos 2x)y = 0 \qquad (2\text{–}73)$$

where a and b are constants. Its general solution may be obtained by the method of integration in series if the substitution

$$\xi = \cos^2 x$$

is made. (73) then reads

$$4\xi(1 - \xi) \frac{d^2y}{d\xi^2} + 2(1 - 2\xi) \frac{dy}{d\xi} + (a - 16b + 32b\xi)y = 0 \qquad (2\text{–}74)$$

[15] Defined by eq. (27).

This equation has a non-essential singularity at $\xi = 0$ and can therefore be developed as a power series about the origin. On inserting

$$y = \sum_\lambda a_\lambda \xi^{\kappa+\lambda}$$

in (74) we obtain

$$2\sum_\lambda (\kappa + \lambda)(2\kappa + 2\lambda - 1)a_\lambda \xi^{\kappa+\lambda-1} - \sum_\lambda [4(\kappa + \lambda)^2 - a + 16b]a_\lambda \xi^{\kappa+\lambda} + 32b\sum_\lambda a_\lambda \xi^{\kappa+\lambda+1} = 0$$

Here a feature arises which was not encountered before; the equation contains *three* different summations instead of two and will therefore lead to a three-term recurrence relation between the coefficients a_λ instead of the two-term relations that occurred in the former instances. This, however, requires no modification of procedure, except that it will force us to advance step by step in the computation of the coefficients. Only the first summation can contribute to the coefficient of $\xi^{\kappa-1}$, which must be zero. Hence the indicial equation is formed as before:

$$\kappa(2\kappa - 1) = 0$$

whence we obtain the two choices: $\kappa = 0, \frac{1}{2}$. Next, we equate to zero the coefficients of ξ^κ, to which the first and second summations contribute. This leads to

$$2(\kappa + 1)(2\kappa + 1)a_1 = (4\kappa^2 - a + 16b)a_0$$

so that

$$a_1 = \frac{1}{2}\,\frac{4\kappa^2 - a + 16b}{(\kappa + 1)(2\kappa + 1)}\,a_0$$

from which a_1 may be determined when the arbitrary constant a_0 is assumed. On equating to zero the coefficient of $\xi^{\kappa+1}$ to which all three summations contribute, one gets

$$2(\kappa + 2)(2\kappa + 3)a_2 - [4(\kappa + 1)^2 - a + 16b]a_1 + 32ba_0 = 0$$

a relation permitting the calculation of a_2, etc. In this way two series can be constructed, one for $\kappa = 0$, the other for $\kappa = \frac{1}{2}$, linear composition of which yields the general solution of (74) and hence of (73). Investigation shows that this solution converges if $|\xi| < 1$.

This general solution, however, is rarely of interest in physics and chemistry, for it is not periodic in x. In most problems leading to Mathieu's equation, x is an angle, so that there is no significant distinction between x and $x + 2n\pi$, where n is an integer. Thus the solutions usually sought must have the property that $y(x + 2\pi n) = y(x)$. The general solution here found, which is of the form

$$\sum_\lambda a_\lambda \xi^\lambda + \xi^{1/2}\sum_\lambda b_\lambda \xi^\lambda \tag{2-75}$$

does not possess this periodicity, as closer investigation would show. Qualitatively this defect is apparent from the failure of the solution to converge for $\xi = \pm 1$, which excludes the values $x = n\pi$ from consideration altogether, as well as from the existence of a branch point of (75) at $\xi = 0$ (arising from the factor $\xi^{1/2}$).

In fact it is impossible to obtain solutions of Mathieu's equation which are periodic and of period 2π in x, unless definite restrictions are placed upon the constant a. It turns out that the latter must be a complicated function of b if the solution is to be periodic.[16]

Floquet's Theorem. An important theorem concerning the general solution of Mathieu's equation, or indeed of any linear differential equation with periodic coefficients which are one-valued functions of x, will now be established. Suppose that $y_1(x)$ and $y_2(x)$ are two linearly independent solutions of (73), so that any particular solution y may be compounded from them by means of two constants A_1 and A_2 as follows:

$$y = A_1 y_1 + A_2 y_2 \tag{2-76}$$

Now it is clear that, if $y_1(x)$ and $y_2(x)$ are solutions of (73), $y_1(x + 2\pi)$ and $y_2(x + 2\pi)$ will also be solutions, for the substitution of $x + 2\pi$ in place of x causes no change in the differential equation. This must, of course, not be interpreted as implying that $y_1(x + 2\pi) = y_1(x)$ and $y_2(x) = y_2(x + 2\pi)$; but it does mean that

$$y_1(x + 2\pi) = \alpha_{11}y_1(x) + \alpha_{12}y_2(x); \quad y_2(x + 2\pi) = \alpha_{21}y_1(x) + \alpha_{22}y_2(x)$$

the α's being constants. Similarly, using (76)

$$\begin{aligned} y(x + 2\pi) &= A_1y_1(x + 2\pi) + A_2y_2(x + 2\pi) \\ &= (A_1\alpha_{11} + A_2\alpha_{21})y_1(x) + (A_1\alpha_{12} + A_2\alpha_{22})y_2(x) \end{aligned}$$

We observe that the constants α are fixed by the choice of y_1 and y_2, but A_1 and A_2 may be chosen at will and still leave y a particular solution of the equation. It is possible to choose them so as to satisfy the equations

$$A_1\alpha_{11} + A_2\alpha_{21} = kA_1; \quad A_1\alpha_{12} + A_2\alpha_{22} = kA_2 \tag{2-77}$$

where k is a constant not within our control, for if eqs. (77) are to be satis-

[16] Cf. Whittaker and Watson, "Modern Analysis," for further details regarding periodic solutions.

fied then k must be subject to the equation

$$\begin{vmatrix} \alpha_{11} - k & \alpha_{21} \\ \alpha_{12} & \alpha_{22} - k \end{vmatrix} = 0 \tag{2-78}$$

But if (77) holds then

$$y(x + 2\pi) = k[A_1y_1(x) + A_2y_2(x)] = ky(x) \tag{2-79}$$

In other words, there exists a particular solution $y(x)$ such that, when x is increased by 2π, the solution itself is multiplied by the constant k. If k were unity, this solution would be periodic.

This result may be expressed in a different way. On putting

$$k = e^{2\pi\mu}, \quad y(x) = e^{\mu x}P(x)$$

eq. (79) reads

$$e^{\mu(x+2\pi)}P(x + 2\pi) = e^{2\pi\mu+\mu x}P(x)$$

so that $P(x)$ turns out to be a periodic function. Thus it is seen that there exists a particular solution of Mathieu's equation of the form

$$y = e^{\mu x}P(x) \tag{2-80}$$

where P is periodic. From here it is only a simple step to obtain a general solution of (73). The differential equation is insensitive to the substitution of $-x$ for x. Hence $e^{-\mu x}P(-x)$ must also be a solution. Moreover, it is an independent solution, since it is not a constant multiple of (80). The complete solution is, therefore, a linear combination of these two:

$$y = c_1e^{\mu x}P(x) + c_2e^{-\mu x}P(-x) \tag{2-81}$$

This result, known as Floquet's theorem, is of interest in some astronomical applications and chiefly in the quantum theory of metals.[17]

Problem. Show that the Schrödinger equation

$$\frac{d^2\psi}{dx^2} + [A + V(x)]\psi = 0,$$

in which A is a constant, and V is a periodic function of x such that $V(x + l) = V(x)$, has solutions of the form

$$\psi = e^{ikx}v(x),$$

where v is also periodic: $v(x + l) = v(x)$.

This is sometimes called Bloch's theorem.[18]

[17] See Seitz, F., "Modern Theory of Solids," McGraw-Hill Book Co., New York, 1940, Chap. VIII.

[18] Bloch, F., *Z. f. Phys.* **52**, 555 (1928).

2.18. Pfaff Differential Expressions and Equations.—The equations of thermodynamics are peculiar inasmuch as they usually occur in the form

$$dW = \sum_{\lambda=1}^{n} X_\lambda dx_\lambda \tag{2-82}$$

where the X_λ are functions of some or all the independent variables x_λ. While (82), which is known as a *Pfaff expression*, is not a differential equation of the customary kind, its importance in chemistry and physics requires consideration. It is for lack of a more adequate place that this material is inserted in the chapter on differential equations. Some of the material which will be developed from a mathematical point of view in this section has already been used in Chapter 1, to which reference should be made for further applications. The equation

$$\sum_{\lambda=1}^{n} X_\lambda dx_\lambda = 0$$

is sometimes called a *total* differential equation or, more generally, a *Pfaff* equation.

Clearly, the expression dW, eq. (82), can be integrated along any path in n-dimensional space, but the integral will *in general* depend on the path of integration. (See Prob. 4, p. 87; also the example in sec. 1.8.) When $\int dW$ depends on the path of integration, it is said to be *incomplete* or *inexact*.

The condition that (82) be a complete differential is

$$dW = df(x_1 x_2 \cdots x_n) \tag{2-83}$$

for then $\int_{\mathbf{r}_1}^{\mathbf{r}_2} dW = f(\mathbf{r}_2) - f(\mathbf{r}_1)$, independently of path. Now

$$df = \sum_\lambda \frac{\partial f}{\partial x_\lambda} dx_\lambda$$

Comparing with (82), we find

$$X_\lambda = \frac{\partial f}{\partial x_\lambda}$$

To state this relation without explicitly introducing the function f, we differentiate it with respect to x_μ, $\mu \neq \lambda$.

$$\frac{\partial X_\lambda}{\partial x_\mu} = \frac{\partial^2 f}{\partial x_\lambda \partial x_\mu}$$

But also

$$\frac{\partial X_\mu}{\partial x_\lambda} = \frac{\partial^2 f}{\partial x_\mu \partial x_\lambda}$$

Hence the necessary condition of "exactness" may be written in the form

$$\frac{\partial X_\lambda}{\partial x_\mu} = \frac{\partial X_\mu}{\partial x_\lambda}, \quad \lambda, \mu = 1 \cdots n \tag{2–84}$$

The reader who is already familiar with vector analysis will note that, if the X_λ are interpreted as components of a *vector* $\mathbf{R}$, (82) may be written

$$dW = \mathbf{R} \cdot d\mathbf{r} \tag{2–82$'$}$$

and the condition of "exactness" becomes

$$\frac{\partial X}{\partial y} - \frac{\partial Y}{\partial x} = \frac{\partial X}{\partial z} - \frac{\partial Z}{\partial x} = \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} = 0$$

or

$$\nabla \times \mathbf{R} = 0 \tag{2–84$'$}$$

These results are of importance in vector analysis where they are usually expressed as follows: The condition that the line integral of $\mathbf{R}$ (expression 82$'$) around any closed curve shall vanish is that $\mathbf{R}$ be the gradient of some scalar function, and this is equivalent to condition (84$'$). (Cf. sec. 4.17.)

We return now to the general situation:

dW is not exact

and distinguish two cases:

A The equation $dW = 0$ has a solution.
B The equation $dW = 0$ does not have a solution.

A. The equation dW = 0 possesses a solution. Leaving aside for the moment all considerations as to when such solutions may be found, we shall first sketch the consequences of the existence of solutions. The equation $dW = 0$ assigns to every point a *direction*, or, what amounts to the same thing, an *element of surface*. (From the point of view of vector analysis this is immediately clear because the relation $\mathbf{R} \cdot d\mathbf{r}$ specifies at every point $(x_1 \cdots x_n)$ the direction $d\mathbf{r}$ which is perpendicular to the vector $\mathbf{R}$.)

When integrated, the equation $dW = 0$ leads to

$$\phi(x_1 x_2 \cdots x_n) = c \tag{2–85}$$

which represents a one-parameter family of surfaces in n-dimensional space. These surfaces consist of the elements specified by $dW = 0$.

We now wish to show that there exists an integrating denominator, $t(x_1 \cdots x_n)$, such that dW/t is an exact differential. The proof is as follows.

Along the surface $\phi(x_1 \cdots x_n) = c$ (cf. Fig. 2–6), we have both $d\phi = 0$ and $dW = 0$. The same is true along a neighboring surface $\phi = c + dc$. Suppose we wish to go from A to C. The change occurring in ϕ is dc, no matter whether the crossing is made at B_1 or at B_2. But the change dW will depend on the path. The important point to note is that no change occurs in W as we pass along either curve; a change can occur only at the *crossing:* dW = function of the point at which the crossing is made. (If $dW \neq 0$ along the two curves, then it would depend on the whole path, not merely on the point of crossing!) Hence $dW = t(B)d\phi$, where B is the *point* of crossing. Hence $dW = t(x_1 \cdots x_n)d\phi$, or

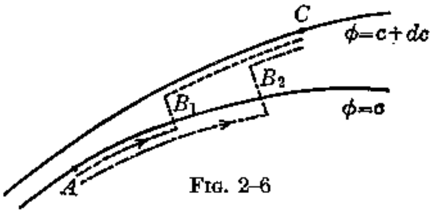

FIG. 2–6

$$d\phi = \frac{dW}{t}$$

But $d\phi$ is an exact differential.

Along the curves ϕ = const., the equation $F(\phi)$ = const. will likewise be satisfied if F represents a unique, single-valued function. If, then, we use $F(\phi)$ in place of ϕ in the preceding analysis, we are led to

$$dF = \frac{dW}{T} \quad \text{instead of} \quad d\phi = \frac{dW}{t}$$

Since, however, $dF = (dF/d\phi)d\phi$, we see that $T = t/(dF/d\phi)$ is also an integrating denominator. It is clear that, if there exists one integrating denominator t for a Pfaff expression, an infinite number of others can be formed by the above rule.

Only the points on the surface $\phi = c$ are connected with A by paths along which $dW = 0$. It is clear that in the neighborhood of A there is an infinite number of points *not* connected with A by such paths. Hence the fact, important in thermodynamics (though somewhat trivial geometrically!):

If the inexact differential dW possesses an integrating denominator t, then there exist, in the neighborhood of every point P, innumerable points which cannot be reached from P along paths for which $dW = 0$.

We now consider the question of *how to find the integrating denominator.*

1. *Case of two variables.* First solve the equation

$$dW = 0; \quad Xdx + Ydy = 0 \tag{2–86}$$

The solution is

$$y = f(x,c), \quad \text{or} \quad \phi(x,y) = c \tag{2–87}$$

Along the curves (87), $\phi_x dx + \phi_y dy = 0$, hence

$$\frac{dy}{dx} = -\frac{\phi_x}{\phi_y} \tag{2–88}$$

But from (86)

$$\frac{dy}{dx} = -\frac{X}{Y}$$

so that

$$\frac{\phi_x}{\phi_y} = \frac{X}{Y}, \quad \text{or} \quad \frac{\phi_x}{X} = \frac{\phi_y}{Y} = u(x,y) \tag{2-89}$$

Now

$$d\phi = \frac{dW}{t} = \phi_x dx + \phi_y dy = uXdx + uYdy = udW$$

Hence

$$t = \frac{1}{u} = \frac{X}{\phi_x} = \frac{Y}{\phi_y} \cdots \tag{2-90}$$

by (89).

2. *Case of three variables.* First solve

$$dW = 0; \quad Xdx + Ydy + Zdz = 0 \tag{2-91}$$

The solution is

$$\phi(x,y,z) = c$$

Along these surfaces, $\phi_x dx + \phi_y dy + \phi_z dz = 0$, hence

$$\left.\frac{dy}{dx}\right|_z = -\frac{\phi_x}{\phi_y}, \quad \left.\frac{dz}{dx}\right|_y = -\frac{\phi_x}{\phi_z}, \quad \left.\frac{dz}{dy}\right|_x = -\frac{\phi_y}{\phi_z}$$

But from (91)

$$\left.\frac{dy}{dx}\right|_z = -\frac{X}{Y}, \quad \left.\frac{dz}{dx}\right|_y = -\frac{X}{Z}, \quad \left.\frac{dz}{dy}\right|_x = -\frac{Y}{Z}$$

Hence

$$\frac{\phi_x}{\phi_y} = \frac{X}{Y}, \quad \frac{\phi_x}{\phi_z} = \frac{X}{Z}, \quad \frac{\phi_y}{\phi_z} = \frac{Y}{Z}$$

or

$$\frac{\phi_x}{X} = \frac{\phi_y}{Y} = \frac{\phi_z}{Z} = u(x,y,z)$$

Now

$$d\phi = \frac{dW}{t} = \phi_x dx + \phi_y dy + \phi_z dz = u(Xdx + Ydy + Zdz)$$

Therefore

$$t = \frac{1}{u} = \frac{X}{\phi_x} = \frac{Y}{\phi_y} = \frac{Z}{\phi_z}$$

Similarly for more than three variables.

We now consider the *condition that the equation*

$$dW = 0$$

shall have a solution. (*Condition of integrability.*)

Suppose a solution of $\sum_{\lambda} X_\lambda dx_\lambda = 0$ exists in the form

$$\phi(x_1 \cdots x_n) = c$$

Then

$$u(x_1 \cdots x_n)X_i = \frac{\partial \phi}{\partial x_i}, \quad i = 1, 2, \cdots n \tag{2-92}$$

Let i, j, k, be different indices. It follows from (92) that

$$\frac{\partial}{\partial x_i}(uX_j) = \frac{\partial^2 \phi}{\partial x_i \partial x_j} = \frac{\partial}{\partial x_j}(uX_i)$$

whence

$$u\left(\frac{\partial X_j}{\partial x_i} - \frac{\partial X_i}{\partial x_j}\right) = X_i \frac{\partial u}{\partial x_j} - X_j \frac{\partial u}{\partial x_i}$$

Similarly,

$$u\left(\frac{\partial X_i}{\partial x_k} - \frac{\partial X_k}{\partial x_i}\right) = X_k \frac{\partial u}{\partial x_i} - X_i \frac{\partial u}{\partial x_k}$$

$$u\left(\frac{\partial X_k}{\partial x_j} - \frac{\partial X_j}{\partial x_k}\right) = X_j \frac{\partial u}{\partial x_k} - X_k \frac{\partial u}{\partial x_j}$$

Multiply the last three equations by X_k, X_j, and X_i, respectively, and add:

$$X_k\left(\frac{\partial X_j}{\partial x_i} - \frac{\partial X_i}{\partial x_j}\right) + X_j\left(\frac{\partial X_i}{\partial x_k} - \frac{\partial X_k}{\partial x_i}\right) + X_i\left(\frac{\partial X_k}{\partial x_j} - \frac{\partial X_j}{\partial x_k}\right) = 0 \tag{2-93}$$

By closer analysis, this equation may be shown to be both necessary and sufficient; it represents the condition of integrability for the Pfaff equation $dW = 0$. In three variables, eq. (93) takes the form

$$\mathbf{R} \cdot \nabla \times \mathbf{R} = 0$$

provided $\mathbf{R}$ is interpreted as the vector having components X_1, X_2, X_3. The total number of equations of the form (93) is equal to the number of triangles that can be formed with n given points as corners; it is therefore $\frac{1}{6}n(n-1)(n-2)$. These equations are therefore not independent.

It is to be observed that, in the case of two variables, eq. (93) is *always* satisfied. Hence every Pfaff equation of the form

$$Xdx + Ydy = 0$$

possesses a solution.

B. The equation dW = 0 does not possess a proper solution, i.e., eq. (93) is not satisfied. For simplicity, we consider only the case of *three* variables, where the solutions can be visualized easily in ordinary space. Generalization to more variables introduces no complications. It will be seen that "improper" solutions of eq. (82) are still possible, but that they represent a greater variety of functions than the proper solutions considered in the preceding paragraphs.

We now choose an *arbitrary* relation

$$\psi(x,y,z) = 0 \tag{2-94}$$

and impose this upon eq. (82), thereby effectively eliminating one degree of freedom. From (94) and its differential form

$$\psi_x dx + \psi_y dy + \psi_z dz = 0$$

the variables z and dz are obtained in terms of x, y, dx, dy, and these solutions are substituted in eq. (82). It will then be of the form

$$X dx + Y dy = 0$$

and this has a solution

$$\phi(x,y) = 0 \tag{2-95}$$

The improper solutions of (82) are said to be those curves which satisfy (94) and (95) simultaneously. They represent, therefore, prescribed curves upon *arbitrary* surfaces. Further investigation would show that every point in the neighborhood of a given point can be reached by a continuous curve satisfying (94) and (95) from the given point, the state of affairs being quite different from that described under **A.**

Problem a. Let $dW = x(dx + dy)$. Compute the integral $\int_{x_1y_1}^{x_2y_2} dW$ along two paths:

1. $x_1y_1 \rightarrow x_2y_1 \rightarrow x_2y_2$.
2. $x_1y_1 \rightarrow x_1y_2 \rightarrow x_2y_2$.

Show that the two results differ by the area enclosed by the two paths of integration.

Problem b. Show that the expression

$$dW = -y dx + x dy + k dz = 0$$

where k is a constant, does not possess an integral.[19]

[19] See Born, M., *Physik. Z.* **22**, 250 (1921).

CHAPTER 3

SPECIAL FUNCTIONS

3.1. Elements of Complex Integration.—In the present chapter the more common functions appearing in physical and chemical theory will be listed and their chief properties will be described. It will be assumed that the reader is familiar with the simpler notions of the calculus of complex variables, in particular with the meaning of the Argand diagram or complex plane. As to notation, the symbol x will be used for a single real variable, while z denotes $x + iy = \rho e^{i\theta}$. We shall also assume without proof the famous theorem of Cauchy which states that, if $f(z)$ is an analytic function of z in a certain region including the point $z = a$, and if $\oint$ denotes the line integral along a closed contour within this domain taken around the point a in a counter-clockwise sense, then

$$\oint f(z)dz = 0 \tag{3-1}$$

and

$$\frac{1}{2\pi i}\oint \frac{f(z)}{z-a}\,dz = f(a) \tag{3-2}$$

From these two equations it is possible to derive the *theorem of residues*, which will now be stated. Suppose that the function $f(z)$ can be expanded in the neighborhood of the point $z = z_0$ in the form

$$f(z) = \frac{a_{-m}}{(z-z_0)^m} + \frac{a_{-m+1}}{(z-z_0)^{m-1}} + \cdots + \frac{a_{-1}}{z-z_0} + a_0 + a_1(z-z_0) + \cdots$$

where m is some finite integer.[1] Then

$$\oint f(z)dz = 2\pi i a_{-1} \tag{3-3}$$

provided the integral is taken counter-clockwise about the point z_0. The coefficient a_{-1} is said to be the *residue* of the function $f(z)$. As a generalization of (3) we note that, if the contour of integration includes other poles

[1] When this expansion is possible, $f(z)$ is said to have a pole of order m at z_0.

at which the function has residues $b_{-1}, c_{-1}, \cdots,$

$$\oint f(z)dz = 2\pi i(a_{-1} + b_{-1} + c_{-1} + \cdots) \tag{3–3a}$$

These theorems are proved in books on complex variables.

Example. To evaluate the integral

$$I = \int_{-\pi}^{\pi} \frac{d\phi}{a + b\cos\phi + c\sin\phi}$$

Let $z = e^{i\phi}$; $\phi = -i\log z$, $d\phi = -i(dz/z)$. Then $\cos\phi = \frac{1}{2}(z + z^{-1})$, $\sin\phi = (1/2i)(z - z^{-1})$.

$$I = -i \oint \frac{dz}{az + \frac{b}{2}(z^2 + 1) + \frac{c}{2i}(z^2 - 1)}$$

the contour being the unit circle about 0. The denominator of the integrand may be written

$$\tfrac{1}{2}(b - ic)z^2 + az + \tfrac{1}{2}(b + ic) = \tfrac{1}{2}(b - ic)\left[z - \frac{1}{b - ic}(-a + R)\right]$$

$$\times \left[z - \frac{1}{b - ic}(-a - R)\right]$$

provided we put

$$\sqrt{a^2 - b^2 - c^2} \equiv R$$

If $a^2 - b^2 - c^2 > 0$ then

$$\left|\frac{1}{b - ic}(-a + R)\right| < 1$$

The other root > 1 and lies outside the unit circle. The residue of the integrand at $z = (-a + R)/(b - ic)$ is

$$\frac{1}{\frac{1}{2}(b - ic)\left[\frac{1}{b - ic}(-a + R) - \frac{1}{b - ic}(-a - R)\right]} = \frac{1}{R}$$

Therefore

$$I = -i \cdot 2\pi i(a^2 - b^2 - c^2)^{-1/2}$$

$$= \frac{2\pi}{\sqrt{a^2 - b^2 - c^2}}$$

3.2. Gamma Function.—The gamma function is a generalization of the factorial $n!$ for non-integral values of n; more specifically, $\Gamma(z)$ is so chosen that, if n is an integer, $\Gamma(n) = (n - 1)!$. A fundamental definition, due to Euler, states

$$\Gamma(z) = \lim_{n\to\infty} \frac{1\cdot 2\cdot 3\cdots(n-1)}{z(z+1)\cdots(z+n-1)}\, n^z \tag{3-4}$$

Several important properties of the Γ-function follow at once from this definition. Since from (4)

$$\Gamma(z+1) = \lim_{n\to\infty} \frac{1\cdot 2\cdots(n-1)}{(z+1)(z+2)\cdots(z+n)}\, n^{z+1}$$

$$\Gamma(z+1) = \lim_{n\to\infty} \frac{zn}{(z+n)}\cdot\frac{1\cdot 2\cdots(n-1)}{z(z+1)\cdots(z+n-1)}\, n^z = z\Gamma(z) \tag{3-5}$$

On the other hand, (4) also shows that

$$\Gamma(1) = \lim_{n\to\infty}\frac{n!}{n!} = 1 \tag{3-6}$$

From (5) and (6) it is at once apparent that, if n is a positive integer,

$$\Gamma(n) = (n-1)! \tag{3-7}$$

as was stated above. It is also evident from the definition (4) that $\Gamma(z)$ becomes infinite at $z = 0, -1, -2$, etc., and that it is an analytic function everywhere else.

It is often useful to represent $\Gamma(z)$ by means of a definite integral. To achieve this, we consider the function

$$F(z,n) \equiv \int_0^n \left(1-\frac{t}{n}\right)^n t^{z-1}dt \tag{3-8}$$

wherein n stands for a positive integer, and the real part of z is taken to be greater than zero in order to insure convergence of the integral. The transformation $\tau = t/n$ converts F into

$$F(z,n) = n^z\int_0^1 (1-\tau)^n\tau^{z-1}d\tau$$

The integral appearing here may be evaluated by repeated partial integrations:

$$\int_0^1 (1-\tau)^n\tau^{z-1}d\tau = \left[(1-\tau)^n\frac{\tau^z}{z}\right]_0^1 + \frac{n}{z}\int_0^1 (1-\tau)^{n-1}\tau^z d\tau$$

The integrated part here vanishes at both limits, and the remainder may again be subjected to a partial integration, yielding

$$\frac{n}{z}\left\{\left[(1-\tau)^{n-1}\frac{\tau^{z+1}}{z+1}\right]_0^1 + \frac{n-1}{z+1}\int(1-\tau)^{n-2}\tau^{z+1}d\tau\right\}$$

The integrated part is again zero. By continuing this process we find

$$F(z,n) = \frac{n(n-1)\cdots 1}{z(z+1)\cdots(z+n-1)} n^z \int_0^1 \tau^{z+n-1} d\tau = \frac{1\cdot 2\cdots n}{z(z+1)\cdots(z+n)} n^z$$

As n approaches infinity, this expression becomes identical with (4); hence

$$\lim_{n\to\infty} F(z,n) = \Gamma(z) \tag{3-9}$$

On the other hand, since $e = \lim_{p\to\infty} (1 + 1/p)^p$ and therefore

$$e^x = \lim_{px\to\infty} (1 + 1/p)^{px} = \lim_{n\to\infty} (1 + x/n)^n$$

the quantity $(1 - t/n)^n$ appearing in (8) approaches the limit e^{-t}. We conclude, therefore, that in view of (8) and (9)

$$\int_0^\infty e^{-t} t^{z-1} dt = \Gamma(z) \tag{3-10}$$

This result is valid, we recall, when the real part of z is greater than zero.

A definition of the Γ-function, or rather its reciprocal, by means of an infinite product has been given by *Weierstrass*. Since it is a useful one, we shall here derive it by simple steps (the rigor of which is not always obvious) from Euler's definition (4). We first note that the product

$$\frac{1}{z}\cdot\frac{1}{z+1}\cdot\frac{2}{z+2}\cdots\frac{n-1}{z+n-1}$$

which appears in (4), may be written $\frac{1}{z}\prod_{m=1}^{n-1}(1 + z/m)^{-1}$, so that (4) becomes

$$\Gamma(z) = \frac{1}{z}\lim_{n\to\infty} n^z \prod_1^n \left(1 + \frac{z}{m}\right)^{-1}$$

or

$$\frac{1}{\Gamma(z)} = z \lim_{n\to\infty} n^{-z} \prod_1^n \left(1 + \frac{z}{m}\right)$$

If we multiply the right-hand side of this equation by unity in the form of

$$\left[\lim_{n\to\infty} e^{(1+1/2+\cdots 1/n)z}\right]\left[\lim_{n\to\infty} \prod_1^n e^{-z/m}\right]$$

we obtain

$$\frac{1}{\Gamma(z)} = z\left[\lim_{n\to\infty} e^{(1+1/2+\cdots 1/n-\log n)z}\right]\left[\lim_{n\to\infty} \prod_1^n \left(1 + \frac{z}{m}\right) e^{-z/m}\right]$$

Now the infinite series: $\lim_{n\to\infty} (1 + \frac{1}{2} + \cdots 1/n - \log n) = C$ converge[s]; it has the value $C = 0.5772\cdots$, known as the *Euler-Mascheroni* constan[t]. Hence

$$\frac{1}{\Gamma(z)} = ze^{Cz}\prod_1^\infty\left(1+\frac{z}{n}\right)e^{-z/n} \qquad (3\text{-}11)$$

which is the Weierstrass definition. It shows, again, that $\Gamma(z)$ has pol[es] at $z = 0, -1, -2$, etc.

A further important property of Γ-functions, namely the relation

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin \pi z} \qquad (3\text{-}12)$$

is readily derived from the Weierstrass definition. First, we recall th[e] theorem:

$$\frac{\sin \pi z}{\pi z} = \prod_1^\infty\left(1-\frac{z^2}{n^2}\right) \qquad (3\text{-}13)$$

which may be proved by an expansion of the infinite product as a sum o[f] powers of z^2. (The details are left as an exercise for the reader.) Fro[m] (11),

$$\Gamma(z)\Gamma(-z) = -\frac{1}{z^2}\prod_1^\infty\left(1+\frac{z}{n}\right)^{-1}\left(1-\frac{z}{n}\right)^{-1}$$

$$= -\frac{1}{z^2}\prod_1^\infty\left(1-\frac{z^2}{n^2}\right)^{-1}$$

$$= -\frac{\pi}{z\sin \pi z} \qquad (3\text{-}14)$$

the last step because of (13). But in view of (5)

$$\Gamma(-z) = -\frac{1}{z}\Gamma(1-z)$$

and this, when inserted in (14), yields (12).

Several other formulas for the derivation of which the reader shoul[d] refer to mathematical treatises,[2] will now be listed without proof.

$$\Gamma(z)\Gamma(z+\tfrac{1}{2}) = 2^{1-2z}\pi^{1/2}\Gamma(2z) \qquad (3\text{-}15)$$

An infinite product of the form

$$\frac{1-a}{1-b}\cdot\frac{2-a}{2-b}\cdot\frac{3-a}{3-b}$$

may be expressed in terms of Γ-functions:

$$\prod_1^\infty\frac{n-a}{n-b} = \frac{\Gamma(1-b)}{\Gamma(1-a)} \qquad (3\text{-}16)$$

[2] Cf., for instance, Whittaker and Watson, p. 235.

Also,

$$\prod_{1}^{\infty} \frac{n(a+b+n)}{(a+n)(b+n)} = \frac{\Gamma(a+1)\Gamma(b+1)}{\Gamma(a+b+1)} \qquad (3\text{-}16a)$$

If m and n are positive constants, not necessarily integral, we have

$$2\int_0^{\pi/2} \cos^{m-1} x \sin^{n-1} x dx = \frac{\Gamma\left(\frac{m}{2}\right)\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{m+n}{2}\right)} \qquad (3\text{-}17)$$

This relation may be modified as follows. Put $m = 2r$, $n = 2s$, and introduce the new variable of integration $\cos^2 x = u$ on the left. The integral will then be converted into

$$\int_0^1 u^{r-1} (1-u)^{s-1} du$$

which is a function of r and s known as the *Eulerian integral of the first kind*, or simply the B-function, and denoted by $B(r,s)$. Eq. (17) may therefore be put in the form

$$B(r,s) = \frac{\Gamma(r)\Gamma(s)}{\Gamma(r+s)} \qquad (3\text{-}17')$$

The logarithmic derivative of the Γ-function is given by

$$\frac{d}{dz} \ln \Gamma(z) = \int_0^\infty \left(\frac{e^{-t}}{t} - \frac{e^{-zt}}{1-e^{-t}}\right) dt \qquad (3\text{-}18)$$

if x = real part of $z > 0$, as was shown by Gauss.

From this result it is possible to obtain an expression for $\ln \Gamma(z)$ which is useful in evaluating $\Gamma(z)$ for large values of z:

$$\ln \Gamma(z) = (z - \tfrac{1}{2}) \ln z - z + \tfrac{1}{2} \ln (2\pi) + O\left(\frac{1}{x}\right) \qquad (3\text{-}19)$$

where $O(1/x)$ represents a series of terms which vanish for large z at least as strongly as $1/x$. For real z, (19) takes the form of *Stirling's* series, when written for Γ instead of its logarithm:

$$\Gamma(x) = e^{-x}x^{x-1/2}(2\pi)^{1/2}\left\{1 + \frac{1}{12x} + \frac{1}{288x^2} - \frac{139}{51840x^3} + \frac{571}{2488320x^4} + \cdots\right\} \qquad (3\text{-}20)$$

It is valid when x is large. This expansion may be used for the approximate evaluation of factorials of large numbers:

$$N! = N\Gamma(N) = e^{-N}N^N(2\pi x)^{1/2}(1 + \cdots \qquad (3\text{-}21)$$