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.

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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. 1., 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

$$
\begin{aligned}
f_{xx} &= \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 z}{\partial x^2} \\
f_{xy} &= \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 z}{\partial x \partial y} \\
f_{yx} &= \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 z}{\partial y \partial x} \\
f_{yy} &= \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 z}{\partial y^2} \quad \text{etc.}
\end{aligned} \tag{1-3}
$$

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

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

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)

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

For the special case,

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

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

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, $u, v, \cdots$

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

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

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

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:

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

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

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

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