PART I

INDUCTIVE FOUNDATIONS OF CLASSICAL THERMODYNAMICS

CHAPTER 1

Mathematical Preliminaries: Functions and Differentials

1.1 PHYSICAL CONCEPTION OF MATHEMATICAL FUNCTIONS AND DIFFERENTIALS

Science consists of interrogating nature by experimental means and expressing the underlying patterns and relationships between measured properties by theoretical means. Thermodynamics is the science of heat, work, and other energy-related phenomena.

An experiment may generally be represented by a set of stipulated control conditions, denoted $x_1, x_2, \ldots, x_n$, that lead to a unique and reproducible experimental result, denoted z. Symbolically, the experiment may be represented as an input–output relationship,

$$\underset{\text{(input)}}{x_1, x_2, \ldots, x_n,} \xrightarrow{\text{experiment}} \underset{\text{(output)}}{z} \tag{1.1}$$

Mathematically, such relationships between independent ($x_1, x_2, \ldots, x_n$) and dependent (z) variables are represented by *functions*

$$z = z(x_1, x_2, \ldots, x_n) \tag{1.2}$$

We first wish to review some general mathematical aspects of functional relationships, prior to their specific application to experimental thermodynamic phenomena.

Two important aspects of any experimentally based functional relationship are (1) its *differential* dz, i.e., the *smallest sensible increment of change* that can arise from corresponding differential changes ($dx_1, dx_2, \ldots, dx_n$) in the independent variables; and (2) its *degrees of freedom* n, i.e., the number of "control" variables needed to determine z uniquely. How "small" is the magnitude of dz (or any of the dx_i) is related to specifics of the experimental protocol, particularly the inherent experimental uncertainty that accompanies each variable in question.

For $n = 1$ ("ordinary" differential calculus), the dependent differential dz may be taken proportional to the differential dx of the independent variable,

$$dz = z'\, dx \tag{1.3}$$

Classical and Geometrical Theory of Chemical and Phase Thermodynamics. By Frank Weinhold

where z' (the total *derivative* of z with respect to x) is evidently related to the differentials dz, dx by the ratio formula

$$z' = \frac{dz}{dx} \tag{1.4}$$

The validity of (1.3), i.e., the existence of the derivative dz/dx in (1.4), is an essential requisite for application of the formalism of differential calculus. It is therefore important that the magnitudes of differentials dz, dx be taken "sufficiently small" (but not "zero," a meaningless and unphysical extrapolation in this context!) for the limiting ratio in (1.4) to have an experimentally well-defined value, within usual limits of experimental precision.

For the general case of n variables, the expression for dz must include corresponding "partial" contributions from each possible differential change dx_i. This is expressed by the important equation

$$\boxed{dz = \sum_{i=1}^{n} \left(\frac{\partial z}{\partial x_i}\right)_{\underline{x}} dx_i = \sum_{i=1}^{n} z_i' \, dx_i} \tag{1.5}$$

where

$$z_i' = \left(\frac{\partial z}{\partial x_i}\right)_{\underline{x}} \tag{1.6}$$

and where the subscript $\underline{x}$ denotes the list of all control variables held constant (i.e., all but the "active" variable dx_i). In general, each "partial" derivative $(\partial z/\partial x_i)_{\underline{x}}$ in (1.5) [like each ordinary derivative z' in (1.3)] is itself a function of all variables on which z depends. Equation (1.5) is referred to as the "chain rule" of partial differential calculus. It represents the most fundamental relationship between differential changes for a system with n degrees of freedom, and often forms the starting point for thermodynamic reasoning.

SIDEBAR 1.1: RECTANGLE EXERCISE

Exercise For a rectangle of sides x, y, find the function for area $A = A(x, y)$, its partial derivatives with respect to x and y, and its differential dA.

Solution The area function is $A(x, y) = xy$, so the partial derivatives are $(\partial A/\partial x)_y = y$ and $(\partial A/\partial y)_x = x$, and the differential is $dA = y\,dx + x\,dy$.

SIDEBAR 1.2: CIRCUMFERENCE EXERCISE

Exercise Suppose that the circumference of the Earth is snugly encircled with a band of 25,000-mile length. If the band is slightly *lengthened* by 10 ft, how high above the surface does it rise? (Does the Earth's precise circumference matter?)

Solution Circumference C and radius R are related by $R = C/2\pi$. To determine the small radial change dR accompanying a change of circumference dC, we need $R' = dR/dC = 1/2\pi$. We can therefore approximate the radial increase ΔR as $\Delta R = R'\Delta C = (1/2\pi)(10 \text{ ft}) \cong 1.59$ ft (independent of C).

The important functional relationships of thermodynamic systems also permit second derivatives to be evaluated. For example, the derivative function $z_i' = z_i'(x_1, x_2, \ldots, x_n)$ of (1.6) can be differentiated with respect to a second variable x_j to give the mixed second derivative of z with respect to x_i and x_j,

$$z_{ij}'' = \left(\frac{\partial z_i'}{\partial x_j}\right)_{\underline{x}} = \frac{\partial^2 z}{\partial x_i \partial x_j} \tag{1.7}$$

As first shown by J. W. Gibbs, the analytical characterization of thermodynamic equilibrium states can be expressed completely in terms of such first and second derivatives of a certain "fundamental equation" (as described in Section 5.1).

Note that differentials (dz) have fundamentally different mathematical character than do functions (such as z, z', z''). The former are inherently "infinitesimal" (microscopic) in scale and carry multivariate dependence on all possible "directions" of change, whereas the latter carry only macroscopic numerical values. Thus, it is mathematically inconsistent to write equations of the form "differential = function" (or "differential = derivative"), just as it would be inconsistent to write equations of the form "vector = scalar" or "apples = oranges." Careful attention to proper balance of thermodynamic equations with respect to differential or functional character will avert many logical errors.

The student of thermodynamics must learn to cope with the functional, differential, and derivative relationships in (1.2)–(1.7) from a variety of formulaic, graphical, and experimental aspects. Let us briefly discuss each in turn.

Formulaic Aspect The student should be familiar with analytical formulas for derivatives z' of common algebraic and transcendental functions z, such as

$$z = x^n,\ z' = nx^{n-1}; \qquad \text{or} \qquad z = u^n,\ z' = nu^{n-1}u' \tag{1.8a}$$

$$z = e^x,\ z' = e^x; \qquad \text{or} \qquad z = e^u,\ z' = e^u u' \tag{1.8b}$$

$$z = \ln x,\ z' = \frac{1}{x}; \qquad \text{or} \qquad z = \ln u,\ z' = \frac{u'}{u} \tag{1.8c}$$

These formulas are also generally sufficient for partial derivatives (because holding some terms *constant* in z can only simplify its differentiation!). Although such formulas may prove useful in certain contexts (such as homework problems based on assumed functional forms of forgiving mathematical simplicity), they are less useful than, for example, graphical or numerical techniques for dealing with realistic experimental data.

Graphical Aspect Functional relationships such as (1.1) and (1.2) can often be most effectively depicted in graphical (or geometric model) form. Innovative graphical methods were developed by Gibbs and others to display the complex thermodynamic relationships of single- and multicomponent chemical systems, as illustrated in Fig. 1.1. For thermodynamic purposes, the ability to "read" equations such as (1.2)–(1.5) through graphical visualization is more important than facility with analytical formulas such as (1.8a–c).

Graphical visualization of a function z or its derivative(s) is similar in the case of ordinary ($n = 1$) and multivariate systems, except that the latter necessarily requires additional dimensions. In a standard 2-dimensional graph, the *height* of the curve at given x_0

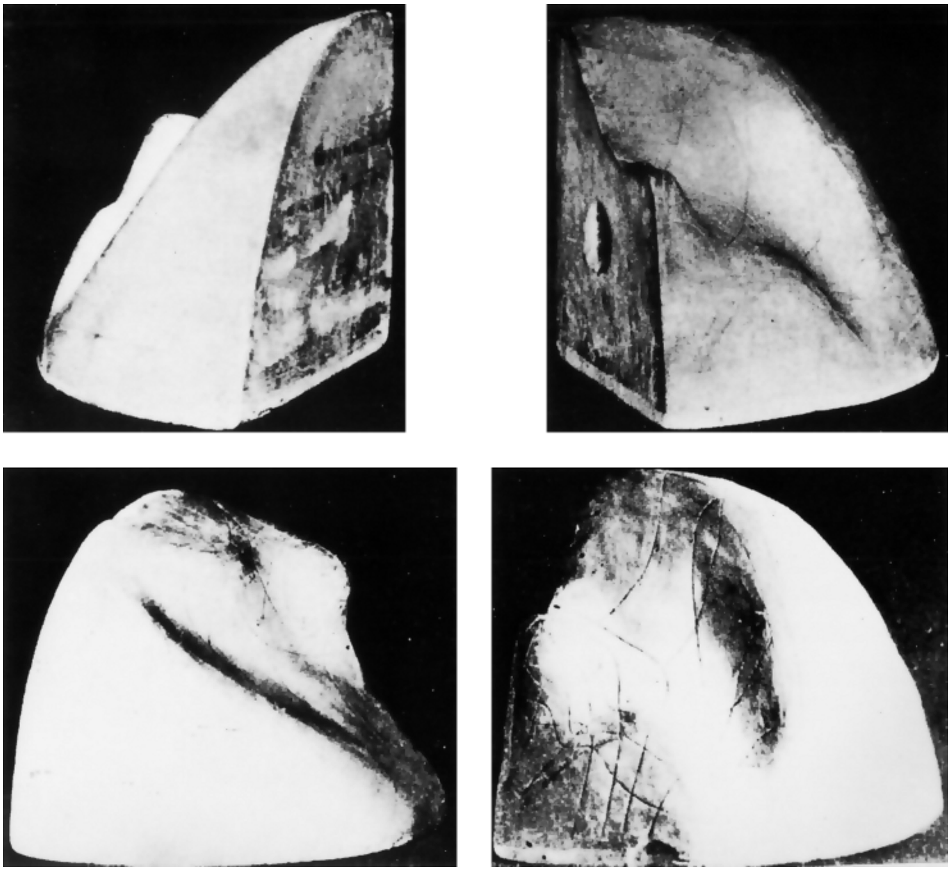
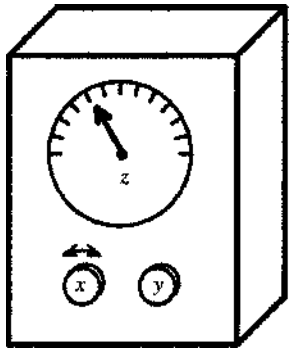


Figure 1.1 Geometrical model depicting thermodynamic properties of water in "Gibbs coordinates." This plaster model, currently in the Beinecke Library at Yale University, was created by noted British physicist James Clark Maxwell as a gift to American thermodynamicist J. Willard Gibbs (see www.public.iastate.edu/∼jolls/ for computer-generated representations by Professor K. R. Jolls).

represents the "strength" of $z = z(x_0)$, whereas the *slope* of the curve is the first derivative $z' = z'(x_0)$ and the *curvature* (variation of slope) is the second derivative $z'' = z''(x^{(0)})$. In a corresponding multidimensional graph, the slope $z_i' = (\partial z/\partial x_i)_{\underline{x}}$ of the surface generally depends on which "direction" dx_i is chosen (different slopes in different directions), and a similar remark applies to the curvature z_{ij}'' for any chosen pair of directions dx_i, dx_j. In general, the slope or curvature in the x direction is independent of that in the y direction, so each partial derivative expresses independent information about the function. Of course, in the thermodynamic context, the partial derivatives generally correspond to experimental "response functions," such as heat capacity or compressibility, that have no literal topographic character. However, it is useful to retain the intuitive topographic imagery (e.g., of a ski hill) to recognize that "slope" and "curvature" must generally depend on the "directions" chosen.

Experimental Aspect Experimental evaluation of a derivative z' (or z_i' in the multivariate case) might be envisioned with the following schematic "z-meter" apparatus:



This apparatus, together with the usual mathematical expression for the limit ratio in (1.4), suggests the experimental protocol for measuring partial derivatives of z. Suppose that the effect of slightly tweaking the control x-dial about its initial setting $x^{(0)}$ by Δx is to give a slight deflection Δz of the z-needle from its initial position $z^{(0)}$. Then the derivative (1.4) can be evaluated as the limit

$$z'\left(x^{(0)}\right) = \left.\frac{dz}{dx}\right|_{x^{(0)}} = \lim_{\Delta x \to \text{“}0\text{”}} \frac{\Delta z}{\Delta x} = \lim_{\Delta x \to \text{“}0\text{”}} \frac{z(x^{(0)} + \Delta x) - z^{(0)}}{\Delta x} \tag{1.9}$$

Here the "0" of the limit means "sufficiently small for the limit to *exist*," which is to be understood more precisely in the context of the experiment. A corresponding z-meter in the multivariable case would have n x_i-dials, each of which is tweaked in turn (holding the remaining $n-1$ dials fixed) to determine the successive partial derivatives z_i, $i = 1, 2, \ldots, n$. It is noteworthy that the multivariate dz carries sufficient information to evaluate *each* of its possible monovariate dx_i derivatives z_i', confirming its status as a more powerful type of mathematical object.

We emphasize that mathematical limiting operations such as (1.9) must make *physical* sense in order to usefully serve thermodynamic applications. The student should always be prepared to make physical estimates of "how small" a sensible differential must be chosen for ratios such as (1.4) or (1.9) to have experimentally well-defined values. (For example, it makes no sense to measure the rainfall rate in a hurricane with a rainfall volume increment corresponding to one droplet, or one molecule, or smaller!) For physical purposes, a differential dz must be sufficiently small for onset of the linear regime expressed by (1.3) or (1.5), but never so small as to raise unjustified concerns about "dividing by zero" in equations such as (1.4) or (1.9).

1.2 FOUR USEFUL IDENTITIES

The special case of $n = 2$ degrees of freedom is often of particular interest. For this purpose, we write the function as $z = z(x, y)$, with the differential dz being given by the usual chain-rule expression

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.10}$$

This is the starting point for the four mathematical identities to be derived below.

(i) Reduction to n = 1 (Single Degree of Freedom) Suppose that the "independent" variables $x = x(u)$, $y = y(u)$ are both simple functions of a single variable u, so that $z = z(u)$ has only "ordinary" derivative dependence on u. What is dz/du? To obtain this ratio, we can simply divide dz (1.10) by du to obtain

$$\boxed{\frac{dz}{du} = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx}{du} + \left(\frac{\partial z}{\partial y}\right)_x \frac{dy}{du}} \tag{1.11}$$

Note closely the distinctions between ordinary (d) and partial (∂) derivatives throughout this formula.

Note also that we employ "physicist's notation" for functions, in which both $z = z(u)$ and $z = z(x, y)$ express how z depends on the variables specified in parentheses (even though the mathematical formulas that express this dependence might be quite different in the two cases). Although somewhat "unmathematical," the chosen notation better expresses the experimental relationship (1.1), in which control variables x_i might be chosen for convenience in many ways, but the target property z is independent of this choice. For example, the volume of a sphere could be equivalently expressed in terms of its measured diameter $[V = V(d) = \pi d^3/6]$ or surface area $[V = V(A) = (\pi^{1/2}/6)A^{3/2}]$, despite the fact that the mathematical dependence (i.e., whether there is a cubic or three-halves power in the chosen measurement argument) is different in the two cases.

(ii) Change of Differentiated Variable Suppose that we re-express $z = z(x, \theta)$ as a function of x and a new variable θ, where the "old" variable $y = y(x, \theta)$ is also expressible in the new independent variables (x, θ). To find the expression for $(\partial z/\partial \theta)_x$ from the "old" differential expression (1.10), we merely divide (1.10) throughout by "$d\theta$ at constant x" [replacing the constrained ratio "$dz/d\theta$ at constant x" on the left-hand side by the proper partial derivative notation, $(\partial z/\partial \theta)_x$, and similarly for both ratios on the right-hand side]:

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

However, the partial derivative $(\partial x/\partial \theta)_x = 0$ (because, at constant x, derivatives of x with respect to *anything* must vanish). The above equation thereby simplifies to

$$\boxed{\left(\frac{\partial z}{\partial \theta}\right)_x = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial \theta}\right)_x} \tag{1.12}$$

Note how the right-hand side has the proper "balance" of differential terms, as though dy can be cancelled from numerator and denominator to give the desired partial derivative.

(iii) Change of Variable Held Constant Under the same change of variables $(x, y) \to (x, \theta)$, we can also obtain the partial derivative $(\partial z/\partial x)_\theta$ (with the new variable θ held constant). Starting again from (1.10), we "divide by dx at constant θ" on both sides (using proper partial derivative notation for the constrained ratios) to obtain

$$\left(\frac{\partial z}{\partial x}\right)_\theta = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial x}\right)_\theta + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_\theta$$

But $(\partial x/\partial x)_\theta = 1$ (since the variations of x with itself are *unity*, no matter what else is constant), so the equation becomes

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_\theta = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_\theta} \tag{1.13}$$

Note that this identity clearly shows that $(\partial z/\partial x)_y \neq (\partial z/\partial x)_\theta$, i.e., that the variable held constant *matters* in these derivatives! (Strictly speaking, a lazy notation such as "$\partial z/\partial x$" has *no meaning whatsoever*!) Although the inconvenient notation of partial derivatives makes it somewhat tedious to keep the inactive (constant) "background" variables in mind, it is important from a physical and pedagogical standpoint that this be done as carefully as possible. (The tedium of this notation is avoided in the geometrical thermodynamics to be presented in Part III.)

SIDEBAR 1.3: CHANGE-OF-VARIABLE EXERCISE

Exercise Suppose the rectangular area A in Sidebar 1.1 is expressed in terms of side x and perimeter P. What are $(\partial A/\partial P)_x$ and $(\partial A/\partial x)_P$?

Solution The new and old variables are related by $P = 2(x + y)$, or

$$y = \tfrac{1}{2}P - x$$

so that

$$\left(\frac{\partial y}{\partial x}\right)_P = -1, \qquad \left(\frac{\partial y}{\partial P}\right)_x = \tfrac{1}{2}$$

From the identity (1.12), we obtain

$$\left(\frac{\partial A}{\partial P}\right)_x = \left(\frac{\partial A}{\partial y}\right)_x \left(\frac{\partial y}{\partial P}\right)_x = (x)\left(\frac{1}{2}\right) = \tfrac{1}{2}x$$

Similarly, from the identity (1.13), we obtain

$$\left(\frac{\partial A}{\partial x}\right)_P = \left(\frac{\partial A}{\partial x}\right)_y + \left(\frac{\partial A}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_P = y + (x)(-1) = \tfrac{1}{2}P - 2x$$

[Of course, in this case, it is also possible to solve explicitly for $A = A(x, P) = \frac{1}{2}Px - x^2$ and differentiate directly, but this "direct" route is often less practical than use of the identities (1.12), (1.13).]

(iv) Jacobi (Cyclic) Identity A provocative identity of great generality and usefulness for $n = 2$ is obtained by considering (1.10) under conditions of constant z (i.e., $dz = 0$). If we then "divide by dx at constant z" (making the usual change of notation from ratio to partial derivative), we obtain

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Noting that $(\partial z/\partial x)_y = 1/(\partial x/\partial z)_y$, we can rewrite the above equation as

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1} \tag{1.14a}$$

Alternately, we can rewrite this identity as

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z/\partial y)_x}{(\partial z/\partial x)_y}} \tag{1.14b}$$

As one can see in (1.14a), the variables (x, y, z) are "cycled" in the three derivatives, each appearing once in the numerator, once in the denominator, and once as the constant variable. The cyclic symmetry makes it easy (and advisable) to commit this identity to memory, even if it can be easily rederived from (1.10) for use as needed.

The identities (1.11)–(1.14) are among the most commonly employed in thermodynamic derivations, because *two* degrees of freedom underlie the important special case of "simple" substances (pure, homogeneous), as will be subsequently described.

1.3 EXACT AND INEXACT DIFFERENTIALS

While the existence of a functional relationship $z = z(x_1, x_2, \ldots, x_n)$ allows its differential dz to be unambiguously determined, the reverse need not be the case. Differentials dz for which *no* corresponding function z exists are called *inexact* (or "imperfect," often marked with a slash: $đ$), whereas those for which z exists are *exact* (or "perfect"). The basic distinction between exact (d-type) and inexact ($đ$-type) differentials lies at the heart of thermodynamic usage of the differential concept, so we must understand clearly how the two cases can be mathematically distinguished. Differentials of heat, for example, are found to belong to the "imperfect" category, whereas those of energy are "perfect."

It might seem that a suitable z (up to an arbitrary constant) could always be generated from a given differential form dz by merely evaluating the integral

$$z \stackrel{?}{=} \int dz$$

This is indeed always possible for a single variable $n = 1$ (ordinary calculus), where the distinction between exact and inexact differentials disappears. However, for $n > 1$, it is clear that integrals over dz must generally depend on the chosen *path* along which the integration is performed. Integrals of multivariate differentials are called *line integrals* (or path integrals) to indicate this distinction from ordinary (monovariate) integrals. For inexact $đz$, the line integral $\int đz$ is *path-dependent* (and therefore not uniquely defined), the signature defect of inexactness. Only in the case of an *exact* differential dz does the indefinite integral $\int dz$ evaluate to a unique function z, independent of the chosen integration path.

Let us first consider this issue in the simple case $n = 2$, with independent variables x, y and dependent variable z. If a well-defined function $z(x, y)$ exists, then dz [of the form (1.10)] is certainly exact. Furthermore, if we evaluate the definite integral from initial (x_1, y_1) to final (x_2, y_2), the result is simply

$$I = \int_{x_1,y_1}^{x_2,y_2} dz = z(x_2, y_2) - z(x_1, y_1) \tag{1.15}$$

The important point is that the final value of the integral depends only on the two endpoints, i.e., the value of the function z at (x_1, y_1) and (x_2, y_2), but not the chosen path of integration (as illustrated in Sidebar 1.4). Moreover, in the special case of a *cyclic* integral (denoted $\oint$), where "initial" and "final" limits coincide, the integral (1.15) necessarily *vanishes* for an exact differential, independent of how the cyclic path is chosen. We can therefore state the following integral criterion for exactness:

Integral criterion: The differential dz is exact if and only if $\oint dz = 0$ for *all* possible paths (1.16a)

A closely related criterion can be stated in graphical terms:

Graphical criterion: The differential dz is exact if and only if its integral $z(x, y) = \int dz$ is *graphable* (1.16b)

This criterion is rather self-evident, because the condition that $z = z(x, y)$ be "graphable" is merely that a *unique* z-value be given any chosen x, y, i.e., that $z = z(x, y)$ satisfies the requirements of a function. However, both criteria require global (integral) information that may be difficult to obtain from local measurements.

SIDEBAR 1.4: SUMMIT TRAIL PROBLEM

Problem On the coast of Hawaii, a sign points to a distant volcano with the information, "Summit: distance = 15.3 km, altitude = 4.2 km." How can one determine which (if either) of the differential quantities dl (distance) or dh (altitude) is exact?

Solution By measuring (e.g., with ruler and altimeter) the differential changes dl, dh and integrating (summing up) their cumulative changes I_l, I_h from coast to summit,

$$I_l = \int_{\text{coast}}^{\text{summit}} dl, \qquad I_h = \int_{\text{coast}}^{\text{summit}} dh$$

one could verify experimentally that I_h is independent of the path chosen to the summit, so that dh is exact, whereas I_l is path-dependent, so that $đl$ is inexact by (1.16a).

As an alternative strategy, one might ask in a local bookshop for an "altitude map" and a "distance map" for Hawaii. A mathematically savvy shopkeeper may reply that the first (a "topo map") is readily available, because altitude is easily graphable in topographic form, whereas the second is not, because distance is inherently a path-dependent, ungraphable quantity. This reply points, by (1.16b), to the same conclusion.

A more convenient differential criterion for exactness was established by Euler. Suppose that the differential dz consists as usual of contributions from dx and dy variations,

$$dz = M(x, y)\,dx + N(x, y)\,dy$$

where the respective coefficients $M = M(x, y)$ and $N = N(x, y)$ are stipulated functions of x and y. We can then state the Euler criterion as follows:

Euler criterion ($n = 2$): The differential $dz = M\,dx + N\,dy$ is exact if and only if

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \text{at every point } x,\ y \tag{1.17}$$

It is easy to recognize that the Euler criterion will be satisfied if the integral or graphical criteria (1.16) are satisfied. Suppose that $z(x, y)$ indeed exists (e.g., displayed as a graph), so that (1.10) is assured. Comparison of (1.10) with the assumed form of the differential then shows that

$$M(x,\ y) = \left(\frac{\partial z}{\partial x}\right)_y, \qquad N(x, y) = \left(\frac{\partial z}{\partial y}\right)_x \tag{1.18}$$

The M-derivative of the Euler criterion (1.17) can therefore be evaluated as

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right)_x = \frac{\partial^2 z}{\partial y\,\partial x} \tag{1.19a}$$

whereas the N-derivative is similarly

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y = \frac{\partial^2 z}{\partial x\,\partial y} \tag{1.19b}$$

The Euler criterion is therefore equivalent to the familiar "mixed partials of a function are equal" rule of calculus. This cross-differentiation rule is also the condition for the function $z(x,\ y)$ to have well-defined (single-valued) first derivatives at each point, and thus to be graphable.

SIDEBAR 1.5: EXACT DIFFERENTIAL EXERCISES

Exercises Use the Euler criterion (1.17) to determine whether each of the following differentials dz is exact or inexact:

(a) $dz = y\,dx + x\,dy$
(b) $dz = y^2\,dx + xy\,dy$
(c) $dz = (y/x)\,dx + \ln(x)\,dy$
(d) $dz = 2x^{-1/3}y^7(y\,dx + 12x\,dy)$

Solutions (a) exact; (b) inexact; (c) exact; (d) exact. To work out the solution of (d) in more detail, we note that

$$M = 2x^{-1/3}y^8, \quad N = 24x^{2/3}y^7$$

so that

$$\left(\frac{\partial M}{\partial y}\right)_x = 16x^{-1/3}y^7 = \left(\frac{\partial N}{\partial x}\right)_y$$

as required for exactness.

SIDEBAR 1.6: ILLUSTRATIVE LINE INTEGRALS

Let us examine the line integrals of two simple *in*exact differentials, namely,

$$đz_1 = y\,dx, \quad đz_2 = x\,dy \tag{S1.6-1}$$

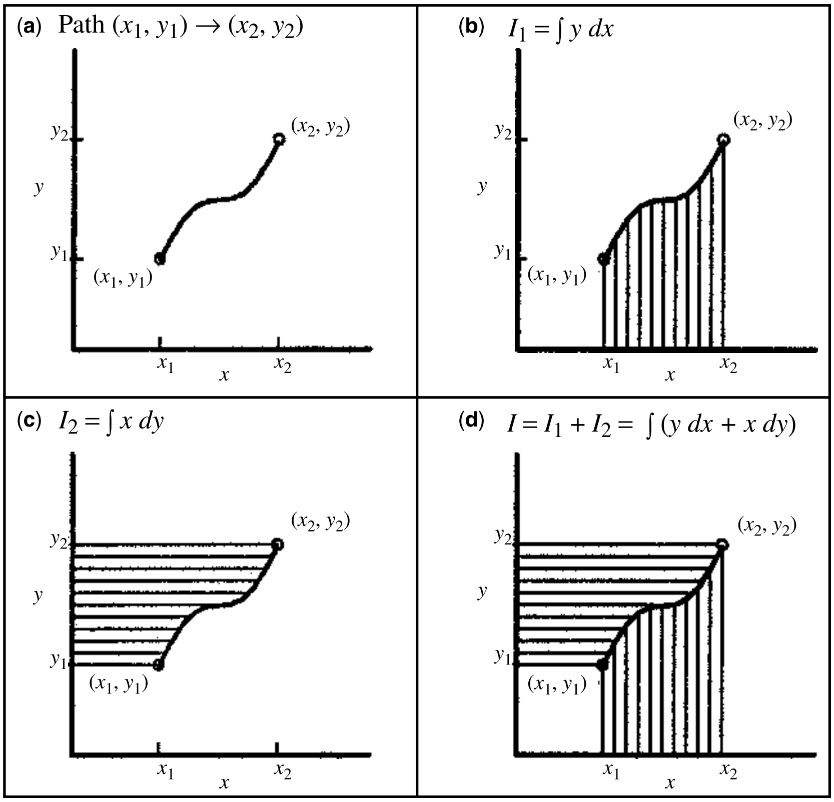
to see their explicit path dependence. We employ the path $y = y(x)$ shown in figure panel (a) to connect the initial point $\mathrm{P} = (x_1, y_1)$ to the final point $\mathrm{Q} = (x_2, y_2)$ in the definite integrals

$$I_1 = \int_{\mathrm{P}}^{\mathrm{Q}} đz_1 = \int_{\mathrm{P}}^{\mathrm{Q}} y\,dx, \qquad I_2 = \int_{\mathrm{P}}^{\mathrm{Q}} đz_2 = \int_{\mathrm{P}}^{\mathrm{Q}} x\,dy \tag{S1.6-2}$$

The first integral I_1 is just the area under the curve $y = y(x)$, as shown by the shaded region in panel (b). Similarly, the second integral I_2 is the area to the left of this curve, as shown by the shaded region in panel (c). Clearly, the values of both I_1 and I_2 are dependent on the chosen path of integration, confirming that $đz_1$ and $đz_2$ are inexact. However, the sum of these differentials, $dz = đz_1 + đz_2 = y\,dx + x\,dy$, is evidently exact [cf. part (a) of Sidebar 1.5]. By inspection, its integral

$$I = \int_{\mathrm{P}}^{\mathrm{Q}} dz = I_1 + I_2 \tag{S1.6-3}$$

is the total area of the shaded L-shaped region in panel (d), which depends on the endpoints (x_1, y_1), (x_2, y_2) but not the connecting path.



For arbitrary n, the more general statement of the Euler criterion can be formulated in terms of a general n-term differential form

$$dz = \sum_{i=1}^{n} R_i dx_i \tag{1.20}$$

with coefficients $R_i = R_i(x_1, x_2, \ldots, x_n)$. The generalization of (1.17) is

Euler criterion (*general n*): The differential $dz = R_1\,dx_1 + R_2\,dx_2 + \cdots + R_n\,dx_n$ (1.21)

is exact if and only if $\left(\frac{\partial R_i}{\partial x_j}\right)_{\underline{x}} = \left(\frac{\partial R_j}{\partial x_i}\right)_{\underline{x}}$ for all $i, j = 1, 2, \ldots, n$

(i.e., mixed partial derivatives are equal for any chosen pair of variables x_i, x_j).

This fundamental relation underlies all thermodynamic descriptions of exact (conserved) differential quantities such as internal energy or entropy, as will be shown in subsequent chapters.

Finally, we briefly mention the concept of an *integrating factor*, a multiplicative factor (L) that converts an inexact differential ($đf$) to an exact differential (dg), namely,

$$L đf = dg \tag{1.22}$$

Integrating factors L may or may not exist for a given $đf$, and if they exist, they are generally non-unique (e.g., $L' = cL$ is also an integrating factor for any constant c). In simple cases, an integrating factor can be guessed "by inspection"; for example, it is easy to see that $L = 1/y$ is an integrating factor for the inexact differential in Sidebar 1.5(b). In more complex cases, the Euler condition (1.21) can be used to convert (1.22) into a differential equation for determining L. In the thermodynamic context, however, the most important integrating factor is that for the differential of heat, and this factor (namely, $L = 1/T$, the inverse temperature) will be obtained from *physical* considerations, rather than, for example, by solving a differential equation.

1.4 TAYLOR SERIES

A common situation in thermodynamics is that some property $z(x)$ and its lower derivatives (z', z'', z''', ...) have been measured at a certain point x_0, and one wishes to use this information to approximate the behavior of the function $z(x_0 + \Delta x)$ in the Δx-neighborhood of x_0. For this purpose, the fundamental *Taylor series* (or MacLaurin series, the special case for $x_0 = 0$) yields approximations that are useful for sufficiently small Δx:

$$z(x_0 + \Delta x) \simeq z(x_0) + z'(x_0)\Delta x + \frac{1}{2!}z''(x_0)(\Delta x)^2 + \frac{1}{3!}z'''(x_0)(\Delta x)^3 + \cdots \tag{1.23}$$

The student of thermodynamics should be able to generate such Taylor series expansions for common algebraic and trigonometric functions.

SIDEBAR 1.7: TAYLOR SERIES EXERCISES

Exercises Use the first few terms of the Taylor series expansion (1.23) to develop small-x approximations for the functions

(a) $z(x) = (1 - x)^{-1}$

(b) $z(x) = \ln(1 + x)$

(c) $z(x) = [\cos(x)]^{-1/2}$

(d) $z(x) = (1 + x^2)^{1/2}$

Solutions

(a) $(1 - x)^{-1} \simeq 1 + x + x^2 + x^3 + \cdots$

(b) $\ln(1 + x) \simeq x - x^2/2 + x^3/3 - \cdots$

(c) $[\cos(x)]^{-1/2} \simeq 1 + x^2/4 + 7x^4/96 + \cdots$

(d) $(1 + x^2)^{1/2} \simeq 1 + x^2/2 - x^4/8 + \cdots$
