

S. M. Blinder<sup>1</sup>  
 University of Michigan  
 Ann Arbor

# Mathematical Methods in Elementary Thermodynamics

**T**hermodynamics is the study of the laws which govern transformations of matter and energy during physical and chemical changes. These laws have their most rigorous and concise formulation in terms of certain specialized mathematical constructs, including partial derivatives, linear differential forms, and line integrals. This paper contains a condensed treatment of some of the mathematical techniques relevant to the study of thermodynamics. It has been the writer's experience in teaching physical chemistry and thermodynamics courses that prior familiarity with this mathematics greatly facilitates the student's subsequent progress. For then he should be able to concentrate more on physical principles, unencumbered by irrelevant mathematical difficulties. In addition, the student will become more aware of the distinction between physical inference and mathematical manipulation in various steps of a derivation.

Mathematics provides a compact language for conveying quantitative ideas. A mathematical symbol can express something which would take many pages to say in words. By use of mathematics, a train of abstract thought can be broken down into a series of short manageable steps. Otherwise, a complex logical sequence might be beyond comprehension.

The stress in our approach is on intuitive conceptualization rather than on mathematical rigor. The reader is referred elsewhere for more rigorous treatment of the topics covered.<sup>2</sup>

## Partial Derivatives

Thermodynamic systems are characterized by certain quantitative physical variables, such as pressure, volume, temperature, internal energy, and entropy. Experience has shown that it is not always possible to vary such quantities at will, but that specification of some results in definite values for others. Mathematically, such a situation is expressed by saying that functional relations exist among the variables. The methods of partial differentiation then become especially appropriate.<sup>3</sup> In this first section we shall re-

view some of the more useful results from the theory of functions of several independent variables.

Consider first a single-valued function  $z$  of two independent variables  $x$  and  $y$ . The functional relation, written  $z = f(x,y)$  or  $z = z(x,y)$ , expresses the fact that for a pair of numbers  $x, y$  (perhaps within a restricted range) there exists a unique value for  $z$ . Geometrically, the functional relation may be represented by a surface in three-dimensional space.<sup>4</sup> If one of the independent variables is constrained to a constant value,  $z$  can be considered a function of the other variable alone. Partial derivatives can then be defined:

$$\left. \begin{aligned} \left(\frac{\partial z}{\partial x}\right)_y &\equiv \lim_{\Delta x \rightarrow 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x} \\ \text{and} \\ \left(\frac{\partial z}{\partial y}\right)_x &\equiv \lim_{\Delta y \rightarrow 0} \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y} \end{aligned} \right\} \quad (1)$$

The subscripts  $x$  or  $y$  can be omitted, but only if there is no ambiguity in what is being kept constant. A partial derivative, like an ordinary derivative, can be interpreted geometrically as the instantaneous slope of

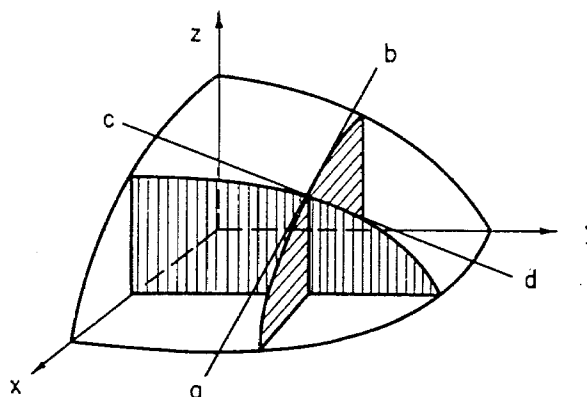


Figure 1. Graphical representation of partial derivative. The curved surface represents  $z = f(x,y)$  in the first quadrant. The horizontally and vertically cross-hatched planes are  $y = \text{constant}$ , and  $x = \text{constant}$ , respectively. Lines  $ab$  and  $cd$  are drawn tangent to the intersection curves;  $(\partial z/\partial x)_y$  is then equal to the slope of  $ab$  and  $(\partial z/\partial y)_x$  is equal to the slope of  $cd$ .

a curve (Fig. 1). Thus  $(\partial z/\partial x)_y$  represents the slope of the curve cut from the surface  $z = f(x,y)$  by a plane  $y = \text{constant}$ ; similarly  $(\partial z/\partial y)_x$  represents the slope in a plane  $x = \text{constant}$ .

Partial derivatives are evaluated by the rules for

<sup>4</sup> For example,  $z = ax + by$  is represented by a plane and  $z = \sqrt{x^2 + y^2}$  by a sphere.

Adapted from Chapter 1 of a physical chemistry textbook to be published by Macmillan Co., New York.

<sup>1</sup> Guggenheim Fellow, 1965-66, at University College, London.

<sup>2</sup> See, for example, WIDDER, D. V., "Advanced Calculus," Prentice-Hall Inc., Englewood Cliffs, N. J., 1947.

<sup>3</sup> See any book on elementary calculus, for example, GRANVILLE, W. A., SMITH, P. E., AND LONGLEY, W. R., "Elements of Differential and Integral Calculus," Ginn and Co., Boston, Mass., 1957.

ordinary differentiation, treating the appropriate variables as constants. For examples, the pressure  $P$  of one mole of an ideal gas is given by

$$P = RT/V \quad (2)$$

where  $V$  is the volume,  $T$  is the absolute temperature, and  $R$  is a universal constant. Treating  $P$  as the dependent variable, we have

$$(\partial P/\partial V)_T = -RT/V^2 \quad (3)$$

$$(\partial P/\partial T)_V = R/V \quad (4)$$

Since the partial derivatives are also functions of the independent variables, they may themselves be differentiated to yield second (and higher) derivatives. These are written

$$\frac{\partial^2 z}{\partial x^2} \equiv \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial x} \right) \quad \text{or} \quad \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial x} \right) \right]_y \quad (5)$$

$$\frac{\partial^2 z}{\partial y \partial x} \equiv \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right) \quad \text{or} \quad \left[ \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right) \right]_x, \text{ etc.}$$

When the function and its derivatives are single-valued and continuous, the order of differentiation in the mixed derivatives is immaterial and

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \quad (6)$$

This is always the case in thermodynamic applications. For the above example.

$$(\partial^2 P/\partial V^2)_T = -2RT/V^3 \quad (7)$$

$$(\partial^2 P/\partial T^2)_V = 0 \quad (8)$$

$$\left( \frac{\partial(\partial P/\partial V)_T}{\partial T} \right)_V = \left( \frac{\partial(\partial P/\partial T)_V}{\partial V} \right)_T = -\frac{R}{V^2} \quad (9)$$

Products of partial derivatives can be manipulated in the same way as products of ordinary derivatives, provided that the same variables are held fixed. Two useful identities are

$$\left( \frac{\partial y}{\partial t} \right)_z \left( \frac{\partial t}{\partial x} \right)_z = \left( \frac{\partial y}{\partial x} \right)_z \quad (10)$$

and

$$\left( \frac{\partial y}{\partial x} \right)_z \left( \frac{\partial x}{\partial y} \right)_z = 1 \quad \text{or} \quad \left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{(\partial y/\partial x)_z} \quad (11)$$

Thus far we have considered changes in  $z(x,y)$  brought about by changing only one of the independent variables at a time. The more general case involves simultaneous variation of  $x$  and  $y$ . This could be represented by the slope of the surface  $z = f(x,y)$  along a direction not, in general, parallel to either coordinate axis. For a function of a single independent variable  $y = f(x)$ , the increment in  $y$  brought about by an infinitesimal change in  $x$  is given by  $dy = (dy/dx)dx$ . When  $z = f(x,y)$ , the increment in  $z$  wrought by simultaneous infinitesimal changes in  $x$  and  $y$  is given by the total differential<sup>5</sup>

<sup>5</sup> This can be shown as follows. Let

$$\Delta z = z(x + \Delta x, y + \Delta y) - z(x, y)$$

Adding and subtracting the quantity  $z(x, y + \Delta y)$  and inserting the factors  $\Delta x/\Delta x$  and  $\Delta y/\Delta y$ , we have

$$\Delta z = \left[ \frac{z(x + \Delta x, y + \Delta y) - z(x, y + \Delta y)}{\Delta x} \right] \Delta x + \left[ \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y} \right] \Delta y$$

Passing to the limit  $\Delta x \rightarrow 0, \Delta y \rightarrow 0$ , the two bracketed quantities become partial derivatives by eqn. (1), while the increments  $\Delta x, \Delta y, \Delta z$  become differentials  $dx, dy, dz$ .

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \quad (12)$$

Extension of the above theory to functions of more than two variables is straightforward. For a function  $u$  of  $r$  variables,  $u = f(x_1, x_2, \dots, x_r)$ , there are  $r$  first partial derivatives  $\partial u/\partial x_1, \partial u/\partial x_2, \dots, \partial u/\partial x_r$ . The total differential is given by

$$du = \left( \frac{\partial u}{\partial x_1} \right) dx_1 + \left( \frac{\partial u}{\partial x_2} \right) dx_2 + \dots + \left( \frac{\partial u}{\partial x_r} \right) dx_r = \sum_{i=1}^r \left( \frac{\partial u}{\partial x_i} \right) dx_i \quad (13)$$

Other properties have obvious analogies and need not be remarked upon further.

Several useful relationships among partial derivatives can be obtained from (12). Suppose, for example, that  $z(x,y) = \text{constant}$ . Then  $dz = 0$  and

$$\left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy = 0 \quad (14)$$

Rearranging we find

$$\frac{dy}{dx} = -\frac{(\partial z/\partial x)_y}{(\partial z/\partial y)_x}$$

But the ratio of  $dy$  to  $dx$  means, in this instance,  $(\partial y/\partial x)_z$ , since  $z$  is constrained to a constant value. Thus we arrive at the important identity

$$\left( \frac{\partial y}{\partial x} \right)_z = -\frac{(\partial z/\partial x)_y}{(\partial z/\partial y)_x} \quad (15)$$

This relationship often enables us to evaluate physical quantities not directly obtainable. To illustrate,

$$\left( \frac{\partial T}{\partial V} \right)_P = -\frac{(\partial P/\partial V)_T}{(\partial P/\partial T)_V} = \frac{RT/V^2}{R/V} = \frac{T}{V} = \frac{P}{R} \quad (16)$$

which agrees with  $(\partial T/\partial V)_P$  calculated directly, after solving the ideal gas equation for  $T$ . Making use of eqn. (11), eqn. (15) can be rearranged to

$$\left( \frac{\partial y}{\partial x} \right)_z \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial x}{\partial z} \right)_y = -1 \quad (17)$$

In the preceding discussion, the relationship among the three variables  $x, y, z$  has been given in explicit form, i.e.,  $z = f(x,y)$ . Solving for  $x$  or  $y$ , one could alternatively write  $x = g(y,z)$  or  $y = h(z,x)$ . Thus the ideal gas equation could be written in any of three ways:

$$P = \frac{RT}{V}, \quad V = \frac{RT}{P}, \quad T = \frac{PV}{R} \quad (18)$$

In many applications it is more desirable to express the functional relationship among  $x, y$ , and  $z$  in a more symmetrical fashion. We accordingly write  $F(x,y,z) = 0$  (for example,  $PV - RT = 0$ ). In this way, the choice of dependent and independent variables is left free. One might choose  $x$  as the dependent variable in one application and  $y$  in another, without needing to reformulate the functional relationship. One would then say, for example, that  $z$  is an implicit function of  $x$  and  $y$  through the relation  $F(x,y,z) = 0$ .

Implicit functions can be applied to the evaluation of derivatives. Consider the total differential of  $F(x,y,z)$  using eqn. (13).

$$dF = \left( \frac{\partial F}{\partial x} \right)_{y,z} dx + \left( \frac{\partial F}{\partial y} \right)_{x,z} dy + \left( \frac{\partial F}{\partial z} \right)_{x,y} dz = 0 \quad (19)$$

This vanishes since  $F$  is a constant ( $=0$ ), thus  $dF = 0$ . Suppose now that we require  $(\partial y/\partial x)_z$ . Since  $z$  is being held constant, we may drop the term in  $dz$ . Thus

$$\left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{z,x} dy = 0 \quad (20)$$

and

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{(\partial F/\partial x)_{y,z}}{(\partial F/\partial y)_{z,x}} \quad (21)$$

This method is useful when it is impossible or inconvenient to solve the implicit relation for  $y$  or  $x$ . To illustrate, suppose we wish to evaluate  $(\partial V/\partial T)_P$  for a gas obeying Dieterici's equation of state

$$P(V-b)e^{a/RTV} = RT \quad (22)$$

where  $a$  and  $b$  are two additional empirical constants. Eqn. (22) cannot be solved in closed form for either  $V$  or  $T$ . But defining

$$F(P, V, T) \equiv P(V-b)e^{a/RTV} - RT = 0 \quad (23)$$

we have<sup>6</sup>

$$(\partial F/\partial T)_{V,P} = -\frac{P(V-b)a}{RT^2V} e^{a/RTV} - R \quad (24)$$

$$(\partial F/\partial V)_{T,P} = P \left[ 1 - \frac{a(V-b)}{RTV^2} \right] e^{a/RTV} \quad (25)$$

Whence by (21), after simplification using (22),

$$\left(\frac{\partial V}{\partial T}\right)_P = -\frac{(\partial F/\partial T)_{V,P}}{(\partial F/\partial V)_{T,P}} = \left(R + \frac{a}{TV}\right) / \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) \quad (26)$$

In most thermodynamic applications, there are alternative choices of the independent variables even if the dependent variable is fixed. We next consider some formulas arising from transformation of variables. Suppose  $z = f(x,y)$  but  $x = x(u,v)$  and  $y = y(u,v)$ . If eqn. (12) is divided by  $du$  and constant  $v$  is specified, we obtain the "chain rule" for two independent variables

$$\left(\frac{\partial z}{\partial u}\right)_v = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v \quad (27)$$

Similarly,

$$\left(\frac{\partial z}{\partial v}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial v}\right)_u + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial v}\right)_u \quad (28)$$

For a function of  $r$  independent variables  $u(x_1, x_2, \dots, x_r)$ , the chain rule generalizes to

$$\frac{\partial u}{\partial t_j} = \sum_{i=1}^r \frac{\partial u}{\partial x_i} \frac{\partial x_i}{\partial t_j} \quad (29)$$

where the  $t_j, j = 1 \dots r$ , are an alternative set of independent variables. It is seen that  $z$  could equally well be regarded as a function of the new variables  $u$  and  $v$ , namely  $z = g(u,v)$ . The total differential can be expressed as

$$dz = \left(\frac{\partial z}{\partial u}\right)_v du + \left(\frac{\partial z}{\partial v}\right)_u dv \quad (30)$$

after writing the total differentials  $dx$  and  $dy$  in terms of  $du$  and  $dv$ , and eliminating among eqns. (12), (27), and (28).

<sup>6</sup> This method of evaluating derivatives is entirely equivalent, in this instance, to differentiating eqn. (23) with respect to  $T$  at constant  $P$ , then solving for  $(\partial V/\partial T)_P$ . This, in effect, retraces the steps in the derivation of eqn. (21).

The following relations among the alternative independent variables are easily proved

$$\left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_y + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_x = 1 \quad (31)$$

$$\left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial v}\right)_u + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial v}\right)_u = 0 \quad (32)$$

Another useful formula involves a "mixed" pair of independent variables, wherein we take  $z = h(x,u)$ . Dividing eqn. (12) by  $dx$  at constant  $u$ , we obtain<sup>7</sup>

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_v + \left(\frac{\partial z}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_u \quad (33)$$

or applying eqn. (15)

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_v - \left(\frac{\partial z}{\partial y}\right)_x \frac{(\partial u/\partial x)_y}{(\partial u/\partial y)_x} \quad (34)$$

Thus if the internal energy  $E$  is given as a function of  $T$  and  $V$ ,  $(\partial E/\partial T)_P$  can easily be evaluated from

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (35)$$

We conclude this section with a brief discussion of homogeneous functions. A function  $f(x_1, \dots, x_r)$  is said to be "homogeneous of degree  $N$ " if

$$f(\lambda x_1, \dots, \lambda x_r) = \lambda^N f(x_1, \dots, x_r) \quad (36)$$

where  $\lambda$  is an arbitrary number. Thus  $f(x,y) = x^2 + y^2$ ,  $f(x,y) = (x^2 + y^2)^{1/2}$ , and  $f(x,y) = y/x$  are homogeneous of degrees 2, 1, and 0, respectively. Euler's theorem on homogeneous functions states that

$$\sum_{i=1}^r \frac{\partial f}{\partial x_i} x_i = N f(x_1, \dots, x_r) \quad (37)$$

when  $f(x_1, \dots, x_r)$  is a homogeneous function of degree  $N$ . To prove (37), we define a new set of independent variables

$$u_i = \lambda x_i, \quad i = 1 \dots r.$$

Next we differentiate each side of (36) with respect to  $\lambda$ . The left-hand side becomes, using the chain rule (29),

$$\frac{\partial f}{\partial \lambda} = \sum_{i=1}^r \frac{\partial f}{\partial u_i} \frac{\partial u_i}{\partial \lambda} \quad (38)$$

while the right-hand side gives simply

$$\frac{\partial f}{\partial \lambda} = N \lambda^{N-1} f(x_1, \dots, x_r) \quad (39)$$

Equating (38) and (39), noting that  $\partial u_i/\partial \lambda = x_i$ , and setting  $\lambda = 1$ , we obtain Euler's theorem, eqn. (37).

Homogeneous functions of degree 0 and 1 are important in thermodynamics, especially in the study of multicomponent systems. Corresponding to the variables  $x_i$  are usually the component mole numbers  $n_i$ . Thermodynamic quantities homogeneous of degree 0 are known as intensive variables. These do not change in value when the mole numbers are increased in proportion, i.e.,

$$f(\lambda n_1, \dots, \lambda n_r) = f(n_1, \dots, n_r) \quad (40)$$

Examples of intensive variables are temperature, pressure, density, viscosity, and index of refraction.

<sup>7</sup> Note the importance of the subscripts here.

Thermodynamic quantities homogeneous of degree 1 are known as extensive variables. These have values proportional to the amount of matter in the system, i.e.,

$$g(\lambda n_1, \dots, \lambda n_r) = \lambda g(n_1, \dots, n_r) \quad (41)$$

Examples of extensive variables are mass, volume, internal energy, entropy, and, of course, the mole numbers themselves. The ratio of two extensive variables is again intensive, for if

$$h(n_1, \dots, n_r) \equiv \frac{g_1(n_1, \dots, n_r)}{g_2(n_1, \dots, n_r)} \quad (42)$$

then

$$h(\lambda n_1, \dots, \lambda n_r) = \frac{g_1(\lambda n_1, \dots, \lambda n_r)}{g_2(\lambda n_1, \dots, \lambda n_r)} = \frac{\lambda g_1(n_1, \dots, n_r)}{\lambda g_2(n_1, \dots, n_r)} = h(n_1, \dots, n_r) \quad (43)$$

Thus density (mass/volume) is intensive, as are various molar quantities, e.g., molar volume (volume/number of moles).

Euler's theorem is useful in relating extensive thermodynamic variables to the corresponding partial molal properties. To illustrate, the volume of a mixture of two liquids at a fixed temperature and pressure depends on the mole numbers  $n_1$  and  $n_2$ ,  $V = V(n_1, n_2)$ . By Euler's theorem, eqn. (37), with  $N = 1$ ,

$$\frac{\partial V}{\partial n_1} n_1 + \frac{\partial V}{\partial n_2} n_2 = V \quad (44)$$

The quantities  $\partial V/\partial n_1$  and  $\partial V/\partial n_2$  (more precisely  $(\partial V/\partial n_1)_{T,P,n_2}$  and  $(\partial V/\partial n_2)_{T,P,n_1}$ ) are known as partial molal volumes (usually abbreviated  $\bar{V}_1$  and  $\bar{V}_2$ ). The first of these represents, for example, the change in volume per mole when a small amount of component 1 is added to a mixture of  $n_1$  moles of component 1 plus  $n_2$  moles of component 2. Other extensive variables likewise have partial molal analogs, the partial molal free energy  $\bar{G}_i$  being especially important in the derivation of thermodynamic principles.

### Differential Expressions

Differential quantities of the type

$$dq(x,y) \equiv X(x,y)dx + Y(x,y)dy \quad (45)$$

known as Pfaff differential expressions, are of central importance in thermodynamics. Two cases are to be distinguished: (1) in which there exists some function  $F(x,y)$  for which eqn. (45) is the total differential, and (2) in which there exists no function of  $x$  and  $y$  which yields (45) upon differentiation. In case (1),  $dq$  is said to be an exact differential (or complete differential or perfect differential) and we can write

$$dF(x,y) = X(x,y)dx + Y(x,y)dy \quad (46)$$

In case (2),  $dq$  is called an inexact (incomplete, imperfect) differential.<sup>8</sup>

A differential expression can be tested for exactness without explicit reference to the function  $F(x,y)$ . Consider first the case in which eqn. (45) is exact and  $F(x,y)$  is known. We can then write the total differential

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \quad (47)$$

But since this differential expansion is unique, eqns. (46) and (47) must be equal and we can identify

$$X(x,y) = \left(\frac{\partial F}{\partial x}\right)_y, \quad Y(x,y) = \left(\frac{\partial F}{\partial y}\right)_x \quad (48)$$

Furthermore,

$$\frac{\partial X}{\partial y} = \frac{\partial^2 F}{\partial y \partial x}, \quad \frac{\partial Y}{\partial x} = \frac{\partial^2 F}{\partial x \partial y} \quad (49)$$

but as discussed earlier, mixed second derivatives of well-behaved functions are independent of the order of differentiation [eqn. (6)]. This leads to Euler's reciprocity relation

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y \quad (50)$$

as a necessary condition for exactness. It is also a sufficient condition and can thus be used as a test for exactness. That is to say, if eqn. (50) applies to  $X(x,y)$  and  $Y(x,y)$ , then eqn. (45) is an exact differential and there exists some function  $F(x,y)$ <sup>9</sup> which satisfies eqn. (46). Note however that the reciprocity criterion neither requires nor identifies the function  $F(x,y)$ .

To illustrate, let us test the differential expression

$$y dx + x dy \quad (51)$$

for exactness. Here  $X(x,y) = y$  and  $Y(x,y) = x$ , and  $\partial X/\partial y = \partial Y/\partial x = 1$ . Thus by eqn. (50), (51) must represent the total differential of some function of  $x$  and  $y$ . The latter is easily identified by inspection as  $F(x,y) = xy$  since  $d(xy) = y dx + x dy$ . Again, consider the differential

$$-(RT/P^2)dP + (R/P)dT \quad (52)$$

The reciprocity condition is again fulfilled since

$$\left[\frac{\partial}{\partial T}\left(-\frac{RT}{P^2}\right)\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{R}{P}\right)\right]_T = -R/P^2 \quad (53)$$

and eqn. (52) is found to represent the total derivative of  $V(P,T) = RT/P$ .

Two differential expressions for which the reciprocity test fails are

$$y dx - x dy \quad (54)$$

and

$$(RT/P)dP - R dT \quad (55)$$

These are consequently inexact differentials. There exist no functions which have total differentials (54) or (55).

An inexact differential expression  $X dx + Y dy$  ( $\partial X/\partial y \neq \partial Y/\partial x$ ) can be converted into an exact one by means of an integrating factor  $M(x,y)$ . In that case  $M(X dx + Y dy)$  becomes exact, i.e.,

$$\frac{\partial(MX)}{\partial y} = \frac{\partial(MY)}{\partial x} \quad (56)$$

For example, (54) can be converted into an exact differential by choosing  $M(x,y) = 1/x^2$ . It is easily verified

<sup>8</sup> Some authors use the notation  $dq$  or  $Dq$  when the differential is inexact but we shall not make this distinction.

<sup>9</sup> As a proof of sufficiency, the function  $F(x,y) = \int X(x,y)dx + \int Y(x,y)dy - \iint \partial(X/\partial y)dx dy$  satisfies eqn. (48) provided that eqn. (50) holds.

that

$$dq = \frac{y dx - x dy}{x^2} = \frac{y}{x^2} dx - \frac{1}{x} dy \quad (57)$$

satisfies (50) and that it is the total differential of  $f(x,y) = -y/x$ . Alternatively, the integrating factor  $1/y^2$  converts (54) to  $d(x/y)$ . Likewise, multiplication by  $-P$  turns (55) into the exact differential (52). An integrating factor can always be found for an inexact differential expression in two independent variables. Evidently, the choice of  $M(x,y)$  is not unique. In fact,  $M(x,y)$  times any function of  $F(x,y)$  is also an integrating factor.

The concept of exact differential is especially important in the formulation of the first and second laws of thermodynamics. Thus, the first law postulates that  $dE \equiv dQ + dW$  is an exact differential even though  $dQ$ , the increment of heat gained by a system, and  $dW$ , the increment of work done on a system, are individually inexact. This constitutes a definition of the internal energy  $E$ . The second law postulates that  $1/T$ , the reciprocal of the absolute temperature, is an integrating factor for  $dQ$ . Thus,  $dS \equiv dQ/T$  is exact, which defines the entropy  $S$ .

Many of the chemical applications of thermodynamics involve more than two independent variables. The linear differential expression in  $r$  independent variables is written

$$dq(x_1, \dots, x_r) = \sum_{i=1}^r X_i(x_1, \dots, x_r) dx_i \quad (58)$$

where each of the  $r$  functions  $X_i$  depends on some or all of the  $x_i$ . Recalling that the total differential of a function  $F(x_1, \dots, x_r)$  of these  $r$  independent variables is given by

$$dF = \sum_{i=1}^r \frac{\partial F}{\partial x_i} dx_i \quad (59)$$

we obtain, when (58) is exact,

$$X_i = \frac{\partial F}{\partial x_i}, \quad i = 1 \dots r \quad (60)$$

From (60) we obtain, in analogy with (50),  $r(r-1)/2$  reciprocity relations (one for each pair  $i, j$ )

$$\frac{\partial X_i}{\partial x_j} = \frac{\partial X_j}{\partial x_i}, \quad i, j = 1 \dots r \quad (61)$$

Conversely, the reciprocity conditions (61) constitute a test for exactness.

As in the case of two independent variables, an integrating factor  $M(x_1, \dots, x_r)$  can convert an inexact differential expression into an exact one. In contrast to the former case, however, an integrating factor does not always exist. A criterion for the existence of an integrating factor for eqn. (58) forms the basis of Carathéodory's formulation of the second law of thermodynamics. Before stating this important principle, we observe that the first order partial differential equation

$$dq = \sum_{i=1}^r X_i dx_i = 0 \quad (62)$$

(known as a Pfaff differential equation) possesses a family of solutions of the form

$$f(x_1, \dots, x_r) = \text{constant} \quad (63)$$

The solutions (63) are here expressed as implicit functional relations among the  $x_i$ . Each solution can be represented by a surface in  $r$ -dimensional space. Carathéodory's principle is now stated without proof:<sup>10</sup>

Let  $f(x_1, \dots, x_r) = \text{constant}$  be one of a family of solutions to the differential equation  $\sum_{i=1}^r X_i dx_i = 0$  and let each solution be represented by a surface. If there exist points  $P'(x_1', \dots, x_r')$  and  $P''(x_1'', \dots, x_r'')$  in  $r$ -dimensional space which *cannot* be connected by some one of these surfaces, then the differential expression  $dQ = \sum_{i=1}^r X_i dx_i$  possesses an integrating factor.

In the thermodynamic application of Carathéodory's principle,  $dQ$  represents an increment of heat gained by a thermodynamic system, each point  $P', P''$ , etc., represents a possible state of the system, and each surface represents a manifold of states accessible one from another by adiabatic processes (those in which no heat is transferred). The experimental fact that there exist thermodynamic states inaccessible by adiabatic means from a given state thus implies the existence of an integrating factor for  $dQ$ . This leads to a definition of entropy and to a compact statement of the second law.

To conclude this section, we describe a method for modifying a differential expression in order to change its independent variables. Such transformations are of considerable importance in chemical thermodynamics. Consider a differential

$$df(x,y) = X(x,y)dx + Y(x,y)dy \quad (64)$$

and define a function

$$g \equiv f - Nx \quad (65)$$

The differential of  $g$  is given by

$$dg = df - Xdx - xdx \quad (66)$$

Substituting (64) for  $df$  we obtain

$$dg = Xdx + Ydy - Xdx - xdx \quad (67)$$

The first and third terms cancel to give

$$dg = Ydy - xdx \quad (68)$$

The differential (68) is appropriate for a function  $g = g(y, X)$  dependent upon  $y$  and  $X$  as independent variables. Analogously one could define

$$h \equiv f - Yy \quad (69)$$

and obtain

$$dh = Xdx - ydY \quad (70)$$

showing that  $h = h(x, Y)$ . It is also possible to carry out a transformation in which both independent variables are changed, for

$$u \equiv f - Nx - Yy \quad (71)$$

has a total differential

$$du = -xdX - ydY \quad (72)$$

showing that  $u = u(X, Y)$ . The above are examples of Legendre transformations, in which one or more of the functions  $X_i$  in eqn. (62) replace the corresponding  $x_i$

<sup>10</sup> For a proof, see MARGENAU, H., and MURPHY, G. M., "Mathematics of Physics and Chemistry," D. Van Nostrand & Co., Inc., Princeton, N. J., 1943, sect. 2.18.

as independent variables.<sup>11</sup> The prescription for these transformations, as exemplified by (65), (69), and (72), is to define a new function  $g$  by subtracting from the original function  $f$  products of the original and the new independent variables.

The most important thermodynamic application of Legendre transformations is based upon Clausius's differential relation,

$$dE = TdS - PdV \quad (73)$$

which is actually a compact statement of the combined first and second laws of thermodynamics. The internal energy  $E$  is evidently a natural function of  $S$  and  $V$ . If a natural function of  $S$  and  $P$  were required, one would define the enthalpy

$$H \equiv E + PV \quad (74)$$

for then

$$dH = dE + PdV + VdP = TdS + VdP \quad (75)$$

On the other hand, transformation to a function of  $T$  and  $V$  would be accomplished by defining the Helmholtz function

$$A \equiv E - TS \quad (76)$$

giving

$$dA = dE - TdS - SdT = -SdT - PdV \quad (77)$$

The remaining choice of independent variables,  $T$  and  $P$ , leads to the Gibbs function or free energy

$$G \equiv E + PV - TS = H - TS = A + PV \quad (78)$$

with total differential

$$dG = -SdT + VdP \quad (79)$$

The four functions,  $E$ ,  $H$ ,  $A$ , and  $G$  are known collectively as thermodynamic potentials. General conditions for chemical equilibrium can be formulated in terms of them.

### Line Integrals

Finite quantities known as line integrals (or curvilinear integrals) derive from differential expressions by integration along curves in space. Before taking up

<sup>11</sup> The student familiar with analytical mechanics will recognize that the Lagrangian and the Hamiltonian functions are connected by a Legendre transformation. The Lagrangian depends upon coordinates and velocities, and the Hamiltonian on coordinates and momenta.

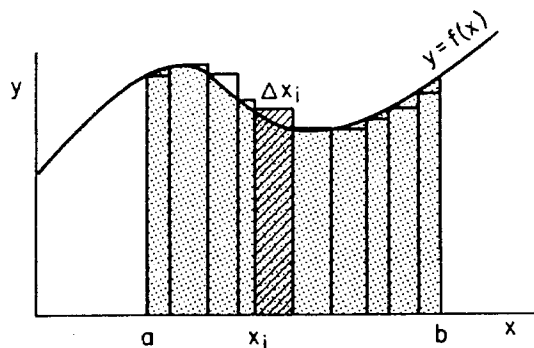


Figure 2. Geometrical representation of the definite integral. The cross-hatched vertical strip has an area  $f(x_i)\Delta x_i$ . The sum of the  $n$  strips with  $i = 0, \dots, n - 1$  approximates the shaded area and approaches it in the limit  $n \rightarrow \infty$ , all  $\Delta x_i \rightarrow 0$ . According to definition (80), the definite integral  $\int_a^b f(x)dx$  equals the shaded area.

line integrals we shall review briefly the theory of ordinary (Riemann) integration for functions of a single independent variable. The definite integral of a continuous function  $f(x)$  is defined by the limit:

$$\int_a^b f(x)dx \equiv \lim_{n \rightarrow \infty} \lim_{\text{all } \Delta x_i \rightarrow 0} \sum_{i=1}^n f(x_i)\Delta x_i \quad (80)$$

where  $\Delta x_i \equiv x_i - x_{i-1}$ ,  $x_0 = a$ , and  $x_n = b$ . The geometrical interpretation of (80), of an integral as an area, is illustrated in Figure 2.

Another fundamental property of the definite integral, connecting the differential and integral calculus is given by

$$\int_a^b f(x)dx = F(b) - F(a) \quad (81)$$

where

$$\frac{dF(x)}{dx} = f(x) \quad (82)$$

This follows easily when the definition of the derivative

$$\lim_{\Delta x_i \rightarrow 0} \frac{F(x_i) - F(x_{i-1})}{\Delta x_i} = f(x_i) \quad (83)$$

is substituted into (80). We have then

$$\sum_{i=1}^n \{F(x_i) - F(x_{i-1})\} = F(b) - F(a) \quad (84)$$

which establishes (81). Also, using (82) in (81),

$$\int_a^b dF(x) = F(b) - F(a) \quad (85)$$

which expresses the definite integral entirely in terms of the boundary values of a function.

An extension of the concept of integration to the case of a function of more than one independent variable involves continuous summation of a differential expression  $dq(x,y)$  along a specified curve. For the case of two independent variables, we define a line integral as follows (Fig. 3)

$$\Delta q_C \equiv \int_C^{x'',y''} \{X(x,y)dx + Y(x,y)dy\} \equiv \lim_{n \rightarrow \infty} \lim_{\text{all } \Delta x_i \rightarrow 0} \lim_{\text{all } \Delta y_i \rightarrow 0} \sum_{i=1}^n \{X(x_i,y_i)\Delta x_i + Y(x_i,y_i)\Delta y_i\} \quad (86)$$

where all the points  $x_i, y_i$  lie on a continuous curve  $C$  connecting  $x', y'(x_0, y_0)$  with  $x'', y''(x_n, y_n)$ . Possibly the best known example of a line integral occurs in mechanics, where the work done on a particle is defined as

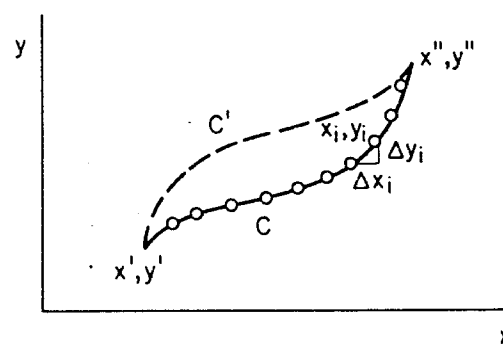


Figure 3. The line integral, as defined in equation (86).

the line integral of force along a trajectory

$$\Delta w = \int \mathbf{F} \cdot d\mathbf{r} = \int \{F_x dx + F_y dy + F_z dz\} \quad (87)$$

A line integral, like a Riemann integral, depends on the sense (direction) of integration. From the definition (86) it follows that

$$\int_{C'}^{x'', y''} dq(x, y) = - \int_C^{x', y'} dq(x, y) \quad (88)$$

It should however be noted that, in contrast to a Riemann integral, a line integral is not represented in any obvious way by an area.

It is readily verified that (86) reduces to a Riemann integral (80) when the path of integration is parallel to either coordinate axis. For example, along the linear path  $y = y_0 = \text{constant}$ , (86) becomes

$$\Delta q_C = \int_{x'}^{x''} X(x, y_0) dx \quad (89)$$

(since  $dy = 0$ ). In general, when the curve  $C$  represents a functional relationship

$$y = g(x) \quad (90)$$

$y$  can be eliminated between (86) and (90) to yield a Riemann integral

$$\Delta q_C = \int_{x'}^{x''} \left\{ X[x, g(x)] + Y[x, g(x)] \frac{dg}{dx} \right\} dx \quad (91)$$

The limits on  $y$  are automatically fulfilled since  $y' = g(x')$  and  $y'' = g(x'')$ . Alternatively one could eliminate  $x$  between (86) and (90) to obtain a Riemann integral over  $y$ .

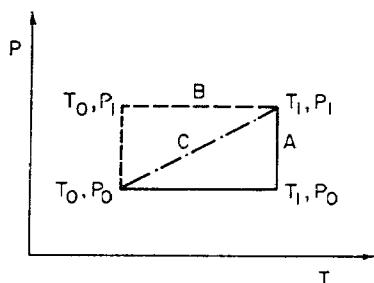


Figure 4. Three possible paths between the states  $T_0, P_0$  and  $T_1, P_1$  of a thermodynamic system.

As an illustration, we integrate the differential expression (55) along the three paths shown in Figure 4. These line integrals

$$\Delta W \equiv \int_{T_0, P_0}^{T_1, P_1} \left\{ \frac{RT}{P} dP - R dT \right\} \quad (92)$$

represent the work done on one mole of an ideal gas in reversible expansion or compression. Along path A, (92) reduces to the sum of two Riemann integrals:

$$\begin{aligned} \Delta W_A &= \int_{T_0, P_0}^{T_1, P_0} \left\{ \frac{RT}{P} dP - R dT \right\} + \\ &\int_{T_1, P_0}^{T_1, P_1} \left\{ \frac{RT}{P} dP - R dT \right\} = RT_1 \int_{P_0}^{P_1} \frac{dP}{P} - \\ &R \int_{T_0}^{T_1} dT = RT_1 \ln \frac{P_1}{P_0} - R(T_1 - T_0) \quad (93) \end{aligned}$$

Along path B we obtain analogously,

$$\Delta W_B = RT_0 \ln \frac{P_1}{P_0} - R(T_1 - T_0) \quad (94)$$

To evaluate  $\Delta W_C$ , we eliminate  $T$  using the equation of the linear path C

$$\frac{T - T_0}{P - P_0} = \frac{T_1 - T_0}{P_1 - P_0} \quad (95)$$

whence

$$T = T_0 + \left( \frac{T_1 - T_0}{P_1 - P_0} \right) (P - P_0) \quad (96)$$

and

$$dT = \frac{T_1 - T_0}{P_1 - P_0} dP \quad (97)$$

Thus

$$\begin{aligned} \Delta W_C &= \int_{P_0}^{P_1} \left\{ \frac{R}{P} \left[ T_0 + \left( \frac{T_1 - T_0}{P_1 - P_0} \right) (P - P_0) \right] - \right. \\ &\left. R \left( \frac{T_1 - T_0}{P_1 - P_0} \right) \right\} dP \\ &= RT_0 \ln \frac{P_1}{P_0} - RP_0 \left( \frac{T_1 - T_0}{P_1 - P_0} \right) \ln \frac{P_1}{P_0} \\ &= \frac{R(T_0 P_1 - T_1 P_0)}{P_1 - P_0} \ln \frac{P_1}{P_0} \quad (98) \end{aligned}$$

Comparing (93), (94), and (98) we see that

$$\Delta W_A \neq \Delta W_B \neq \Delta W_C. \quad (99)$$

Thus the line integral depends in general on the path of integration.

If, on the other hand, we integrate the differential expression (52)

$$\Delta V = \int_{T_0, P_0}^{T_1, P_1} \left\{ \frac{R}{P} dT - \frac{RT}{P^2} dP \right\} \quad (100)$$

along the same three paths, we find

$$\Delta V_A = \Delta V_B = \Delta V_C = \frac{RT_1}{P_1} - \frac{RT_0}{P_0} = V_1 - V_0 \quad (101)$$

[using  $V$  from the ideal gas law (2)]. In fact, eqn. (100) evaluated along any path between  $T_0, P_0$  and  $T_1, P_1$  gives the same result. The independence of path stems from the fact that we are integrating an exact differential (52) [whereas (92) contains the inexact differential (55)].

To prove the above statement, let  $dq$  in (86) be the total differential of a function  $F(x, y)$ . Then using (48) we can write

$$\Delta F(x_i, y_i) = X(x_i, y_i) \Delta x_i + Y(x_i, y_i) \Delta y_i \quad (102)$$

where  $\Delta F(x_i, y_i)$  means  $F(x_i, y_i) - F(x_{i-1}, y_{i-1})$ . Substituting (102) in (86) we find

$$\begin{aligned} \Delta q_C &= \int_{C'}^{x'', y''} dF(x, y) = \lim_{n \rightarrow \infty} \sum_{i=1}^n \Delta F(x_i, y_i) \\ &= F(x'', y'') - F(x', y') \quad (103) \end{aligned}$$

independent of the path C. Note the correspondence between eqns. (103) and (85). In both instances, the value of the integral depends only on its end points. Conversely, it can be shown that, if a line integral is independent of path, the differential must be exact.

Of particular importance are line integrals around closed paths, in which case the initial and final points may be thought to coincide. For cyclic paths, the integral sign is usually written  $\oint$ . The closed curve is by convention traversed in the counterclockwise

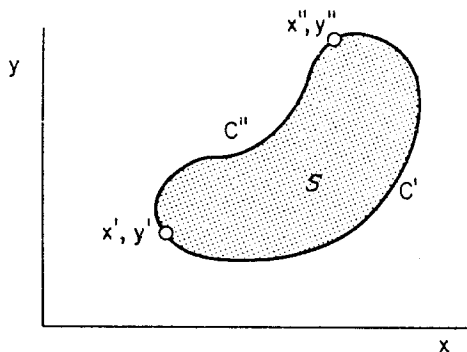


Figure 5. Line integral around closed path, as defined in equations (105) and (106).

sense. If  $dq(x,y)$  is an exact differential, then

$$\oint_C dq(x,y) = \oint_C \{X(x,y)dx + Y(x,y)dy\} = 0 \quad (104)$$

for an arbitrary closed path  $C$ . This is easily proved, for dividing  $C$  into two segments  $C'$  and  $C''$  connecting  $x',y'$  with  $x'',y''$  (Fig. 5), we have

$$\oint_C dq = \int_{C'}^{x'',y''} dq + \int_{C''}^{x',y'} dq \quad (105)$$

Both since both integrals on the right hand side are independent of path by eqn. (103), and since one is the negative of the other by eqn. (88), we obtain eqn. (104). When  $dq(x,y)$  is inexact, however, the cyclic integral is, in general, different from zero.

A final connection between differential expressions and line integrals is provided by Green's theorem<sup>12</sup>

$$\oint_C \{X(x,y)dx + Y(x,y)dy\} = \iint_S \left[ \left( \frac{\partial Y}{\partial x} \right)_y - \left( \frac{\partial X}{\partial y} \right)_x \right] dx dy \quad (106)$$

where the right hand side represents a double Riemann integral over the area  $S$  enclosed by the curve  $C$ . If Euler's reciprocity condition (50) holds for  $dq(x,y)$ , then the right hand side of (106) vanishes and (104) follows. Conversely if the left hand side of (106) vanishes for arbitrary  $C$ , then the integrand of the right hand side must vanish and (50) follows.

By Green's theorem, certain cyclic line integrals can be represented by areas. To illustrate, a differential element of work done on a system in a reversible process is given by

$$dW = -PdV \quad (107)$$

using eqn. (106) with  $P$  and  $V$  as independent variables (noting that the coefficient of  $dP$  is 0), we find, for the work done in a cyclic reversible process

$$\Delta W_C = - \oint_C PdV = - \iint_S dPdV \quad (108)$$

The right hand side is clearly equal to the negative of the area  $S$  enclosed by the path  $C$ . Note that the non-vanishing of (108) shows  $dW$  to be an inexact differential. Actually, since the  $dP$  term is lacking in eqn. (107),  $\Delta W$  can be represented by an area even for a non-cyclic process. Thus we may write

<sup>12</sup> For proof see, for example, KAPLAN, W., "Advanced Calculus," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1952, p. 239ff.

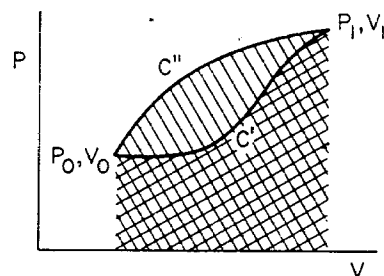


Figure 6. Representation of work as area.<sup>8</sup>

$$\Delta W_C = - \int_{C'}^{P_1, V_1} PdV = - \int_{V_0}^{V_1} P(V)dV \quad (109)$$

where the path  $C$  determines  $P$  as a function of  $V$ . Since the right hand side is a Riemann integral it can be represented by an area (Fig. 6).

To summarize several of the interrelationships dealt with in this section, for a Pfaff differential expression

$$dq(x,y) \equiv X(x,y)dx + Y(x,y)dy$$

any of the following statements implies the other two: (1) There exists a function  $F(x,y)$  whose total derivative is  $dq(x,y)$  ( $dq$  is an exact differential); (2)  $(\partial X/\partial y)_x = (\partial Y/\partial x)_y$  (Euler's reciprocity relation); and (3)  $\oint_C dq(x,y) = 0$  for an arbitrary closed path  $C$ .

Many of the mathematical abstractions encountered in this paper have obvious analogs in thermodynamic terms. A point in the  $xy$  plane can represent the state of a thermodynamic system having two degrees of freedom. The independent variables can be chosen from among  $P$ ,  $V$ ,  $T$ ,  $E$ ,  $S$ , etc. A function  $F(x,y)$  corresponds to another thermodynamic variable. It is called a function of state since it is uniquely determined by the state of the system. An exact differential represents an increment in a function of state whereas an inexact differential represents an increment in a thermodynamic quantity *not* a function of state. A curve on the  $xy$  plane can represent an equilibrium process, that is, a sequence of states between some initial and final states. A line integral represents the change in a thermodynamic quantity in the course of a process. If that quantity is a function of state, the line integral is independent of path. This is entirely reasonable since the change in a function of state is simply the difference between its initial and final values. A line integral around a closed path represents a cyclic process, one which returns the system to its initial state. Clearly, such a process leaves a function of state unchanged.

<sup>13</sup> The work done in traversing the path  $C'$  from  $P_0, V_0$  to  $P_1, V_1$  is equal to the negative of the area under  $C'$ .

$$\Delta W_{C'} = - \int_{C'}^{P_1, V_1} PdV$$

The work done in returning to the original state via path  $C''$  is equal to the area under  $C''$ .

$$\Delta W_{C''} = - \int_{C''}^{P_0, V_0} PdV = \int_{C''}^{P_0, V_0} PdV$$

The net work done in the cyclic process is given by

$$\Delta W_C = \Delta W_{C'} + \Delta W_{C''}$$

and is equal to the area enclosed by the cyclic path. The last result also follows from Green's theorem (106).