Thermodynamics 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 them 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.²

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.² 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 \( z = f(x, y) \) 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.⁴ 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:

\[
\frac{\partial z}{\partial x} = \lim_{\Delta x \to 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x}
\]

and

\[
\frac{\partial z}{\partial y} = \lim_{\Delta y \to 0} \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y}
\]

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

Partial derivatives are evaluated by the rules for

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⁴ For example, \( z = ax + by \) is represented by a plane and \( z = \sqrt{x^2 + y^2} \) by a sphere.
ordinary differentiation, treating the appropriate variables as constants. For examples, the pressure \( P \) of one mole of an ideal gas is given by
\[
P = RT/V
\]
(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
\[
(\partial P/\partial V)_T = -RT/V^2
\]
(3)
\[
(\partial P/\partial T)_V = R/V
\]
(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
\[
\frac{\partial^2 P}{\partial x^2} = \frac{\partial}{\partial x} \left( \frac{\partial P}{\partial x} \right) \quad \text{or} \quad \left[ \frac{\partial}{\partial x} \left( \frac{\partial P}{\partial x} \right) \right]_y
\]
(5)
\[
\frac{\partial^2 P}{\partial y^2} = \frac{\partial}{\partial y} \left( \frac{\partial P}{\partial y} \right) \quad \text{or} \quad \left[ \frac{\partial}{\partial y} \left( \frac{\partial P}{\partial y} \right) \right]_x,
\]
etc.
When the function and its derivatives are single-valued and continuous, the order of differentiation in the mixed derivatives is immaterial and
\[
\frac{\partial^2 P}{\partial x \partial y} = \frac{\partial^2 P}{\partial y \partial x}
\]
(6)
This is always the case in thermodynamic applications. For the above example,
\[
(\partial^2 P/\partial V^2)_T = -2RT/V^3
\]
(7)
\[
(\partial^2 P/\partial T^2)_V = 0
\]
(8)
\[
\left( \frac{\partial^2 P}{\partial V \partial T} \right)_T = \left( \frac{\partial^2 P}{\partial T \partial V} \right)_T = -\frac{R}{V^2}
\]
(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
\[
\frac{\partial y}{\partial x} \left( \frac{\partial x}{\partial y} \right) = \left( \frac{\partial y}{\partial x} \right)_z
\]
(10)
and
\[
\frac{\partial y}{\partial x} \left( \frac{\partial x}{\partial y} \right)_y = 1 \quad \text{or} \quad \frac{\partial x}{\partial y} \left( \frac{\partial y}{\partial x} \right)_y = 1
\]
(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 \( dy = (dy/dx) \Delta x \). When \( z = f(x,y) \), the increment in \( z \) brought by simultaneous infinitesimal changes in \( x \) and \( y \) is given by the total differential\(^8\)

\[\Delta z = \left[ \frac{\partial z}{\partial x} \Delta x + \frac{\partial z}{\partial y} \Delta y \right] \Delta x + \left[ \frac{\partial z}{\partial x} \Delta x + \frac{\partial z}{\partial y} \Delta y \right] \Delta y \]

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

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\( dP = \left( \frac{\partial P}{\partial x} \right)_y \, dx + \left( \frac{\partial P}{\partial y} \right)_x \, dy + \left( \frac{\partial P}{\partial z} \right)_{x,y} \, dz = 0 \)
(19)
This vanishes since \( F \) is constant \((=0)\), thus \( dF = 0 \).

Suppose now that we require \( \partial y / \partial x \). Since \( z \) is being held constant, we may drop the term in \( dz \). Thus

\[
\left( \frac{\partial F}{\partial x} \right)_{z} + \left( \frac{\partial F}{\partial y} \right)_{x} \, dy = 0
\]  

and

\[
\left( \frac{\partial y}{\partial x} \right)_{z} = - \frac{\left( \frac{\partial F}{\partial x} \right)_{z}}{\left( \frac{\partial F}{\partial y} \right)_{x}}
\]  

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 \( \partial V/\partial T \) for a gas obeying Diericci's equation of state

\[
P(V - b)e^{nu} = RT
\]

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

\[
F(P, V, T) \equiv P(V - b)e^{nu} - RT = 0
\]

we have

\[
\left( \frac{\partial F}{\partial V} \right)_{T} = - \frac{P(V - b)a}{RT^2} e^{nu} - R
\]

and

\[
\left( \frac{\partial F}{\partial T} \right)_{V} = P \left[ 1 - \frac{a(V - b)}{RT^2} \right] e^{nu}
\]

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

\[
\left( \frac{\partial V}{\partial T} \right)_{P} = - \left( \frac{\partial F}{\partial T} \right)_{V} \left( \frac{\partial F}{\partial V} \right)_{P} = \left( \frac{\partial F}{\partial V} \right)_{P} \left( \frac{RT}{V} - a \right)
\]

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 \( z = x(u, t) \) and \( y = y(u, t) \).

If eqn. (12) is divided by \( du \) and constant \( v \) is specified, we obtain the "chain rule" for two independent variables

\[
\left( \frac{\partial r}{\partial x} \right)_{u} = \left( \frac{\partial r}{\partial x} \right)_{u} \frac{\partial y}{\partial u} + \left( \frac{\partial r}{\partial y} \right)_{u} \frac{\partial y}{\partial u}
\]

Similarly,

\[
\left( \frac{\partial r}{\partial y} \right)_{u} = \left( \frac{\partial r}{\partial x} \right)_{u} \frac{\partial y}{\partial u} + \left( \frac{\partial r}{\partial y} \right)_{u} \frac{\partial y}{\partial u}
\]

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

\[
\frac{\partial u}{\partial l} = \sum_{i=1}^{r} \frac{\partial u}{\partial x_i} \frac{\partial x_i}{\partial l}
\]

where the \( t, j = 1 \ldots r \), 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

\[
dz = \left( \frac{\partial z}{\partial x} \right)_{y} \, dx + \left( \frac{\partial z}{\partial y} \right)_{u} \, dy
\]

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

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The following relations among the alternative independent variables are easily proved

\[
\left( \frac{\partial u}{\partial x} \right) \left( \frac{\partial x}{\partial u} \right) + \left( \frac{\partial u}{\partial y} \right) \left( \frac{\partial y}{\partial u} \right) - 1 = 0
\]

\[
\left( \frac{\partial u}{\partial x} \right) \left( \frac{\partial y}{\partial u} \right) + \left( \frac{\partial u}{\partial y} \right) \left( \frac{\partial y}{\partial u} \right) = 0
\]

Another useful formula involves a "mixed" pair of independent variables, wherein we take \( z = h(x, y) \). Dividing eqn. (12) by \( dx \) at constant \( u \), we obtain

\[
\left( \frac{\partial x}{\partial z} \right)_{v} = \left( \frac{\partial x}{\partial u} \right) + \left( \frac{\partial x}{\partial y} \right) \left( \frac{\partial y}{\partial u} \right)
\]

or applying eqn. (15)

\[
\left( \frac{\partial x}{\partial z} \right)_{v} = \left( \frac{\partial x}{\partial u} \right) - \left( \frac{\partial x}{\partial y} \right) \left( \frac{\partial y}{\partial u} \right)
\]

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

\[
\left( \frac{\partial E}{\partial T} \right)_{V} = \left( \frac{\partial E}{\partial V} \right)_{T} + \left( \frac{\partial E}{\partial T} \right)_{V} \left( \frac{\partial T}{\partial V} \right)
\]

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

\[
f(\lambda x_1, \ldots, \lambda x_r) = \lambda^N f(x_1, \ldots, x_r)
\]

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

\[
\sum_{i=1}^{r} \frac{\partial f}{\partial x_i} = N f(x_1, \ldots, x_r)
\]

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

\[
u_i = \lambda x_i, \quad i = 1 \ldots r
\]

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

\[
\frac{\partial f}{\partial \lambda} = \sum_{i=1}^{r} \frac{\partial f}{\partial x_i} \frac{\partial x_i}{\partial \lambda}
\]

while the right-hand side gives simply

\[
\frac{\partial f}{\partial \lambda} = \lambda^{N-1} f(x_1, \ldots, x_r)
\]

Equating (38) and (39), noting that \( \partial x_i / \partial x \lambda = x_i \) 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.,

\[
f(\lambda n_1, \ldots, \lambda n_r) = f(n_1, \ldots, n_r)
\]

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

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4 This method of evaluating derivatives is entirely equivalent, in this instance, to differentiating eqn. (28) with respect to \( T \) at constant \( P \), then solving for \( \partial V/\partial T \). This, in effect, retraces the steps in the derivation of eqn. (21).

7 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.,

\[ y(\lambda n_1, \ldots, \lambda n_r) = \lambda y(n_1, \ldots, n_r) \quad (41) \]

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

\[ h(n_1, \ldots, n_r) = \frac{y_1(n_1, \ldots, n_r)}{y_2(n_1, \ldots, n_r)} \quad (42) \]

then

\[ h(\lambda n_1, \ldots, \lambda n_r) = \frac{y_1(\lambda n_1, \ldots, \lambda n_r)}{y_2(\lambda n_1, \ldots, \lambda n_r)} = \frac{y_1(n_1, \ldots, n_r)}{y_2(n_1, \ldots, n_r)} = h(n_1, \ldots, n_r) \quad (43) \]

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 \( \tilde{V}_1 \) and \( \tilde{V}_2 \)). 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 \( \tilde{G}_1 \), being especially important in the derivation of thermodynamic principles.

**Differential Expressions**

Differential quantities of the type

\[ dq(x,y) = X(x,y)dx + Y(x,y)dy \quad (45) \]

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.\(^8\)

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,

\[ \frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x} = \frac{\partial f}{\partial x} \frac{\partial f}{\partial y} \quad (49) \]

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

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

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 \( F(x,y) \) 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

\[ y \, dx + z \, dy \quad (51) \]

for exactness. Here \( X(x,y) = y \) and \( Y(x,y) = z \), 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

\[ -(RT/P)dP + (R/P)dT \quad (52) \]

The reciprocity condition is again fulfilled since

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

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 \( X \, dx + Y \, dy \) 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

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\(^8\) Some authors use the notation \( dq \) or \( Dq \) when the differential is inexact but we shall not make this distinction.
satisfies (50) and that it is the total differential of
that it is the total differential of

\[ dy = \frac{y}{x} \, dx - \frac{z}{x^2} \, dy = \frac{y}{x} \, dx - \frac{1}{x} \, dy \]  
(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 \( F(x, y) \) 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

\[ dE = dQ + dW \]
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, \( dS = dQ/T \) 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

\[ dy = \sum_{i=1}^{r} X_i \, dx_i \]  
(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 \( F(x_1, \ldots, x_r) \) of these \( r \) independent variables is given by

\[ dF = \sum_{i=1}^{r} \frac{\partial F}{\partial x_i} \, dx_i \]  
(59)

we obtain, when (58) is exact,

\[ X_i = \frac{\partial F}{\partial x_i} \quad i = 1 \ldots r \]  
(60)

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

\[ \frac{\partial X_j}{\partial x_i} = \frac{\partial X_i}{\partial x_j} \quad i, j = 1 \ldots r \]  
(61)

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

As in the case of two independent variables, an integrating factor \( M(x_1, \ldots, x_r) \) 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

\[ dq = \sum_{i=1}^{r} X_i \, dx_i = 0 \]  
(62)

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

\[ f(x_1, \ldots, x_r) = \text{constant} \]  
(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.\(^\text{16}\)

Let \( f(x_1, \ldots, x_r) = \text{constant} \) 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 \( P_1(x_1', \ldots, x_r') \) and \( P_2(x_1', \ldots, x_r') \) 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 \( P_1, P_2, \text{etc.} \), 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

\[ df(x, y) = X(x, y) \, dx + Y(x, y) \, dy \]  
(64)

and define a function

\[ g = f - X \]  
(65)

The differential of \( g \) is given by

\[ dg = df - X \, dx - zdX \]  
(66)

Substituting (64) for \( df \) we obtain

\[ dg = X \, dx + Y \, dy - X \, dx - zdX \]  
(67)

The first and third terms cancel to give

\[ dg = Y \, dy - zdX \]  
(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

\[ h = f - Y \]  
(69)

and obtain

\[ dh = X \, dx - y \, dY \]  
(70)

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

\[ u = f - X - Y \]  
(71)

has a total differential

\[ du = -X \, dx - y \, dY \]  
(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 \( x_i \).

as independent variables.\(^\text{11}\) 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 dif-
fential relation,
\[ dE = TdS - PdV \]  
which is actually a compact statement of the com-
bined 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
\[ H = E + PV \]  
for then
\[ dH = dE + PdV + VdP = TdS + VdP \]  
On the other hand, transformation to a function of \(T\)
and \(V\) would be accomplished by defining the Helmholtz
function
\[ A = E - TS \]  
giving
\[ dA = dE - TdS - SdT = -SdT - PdV \]  
The remaining choice of independent variables, \(T\) and \(P\),
leads to the Gibbs function or free energy
\[ G = E + PV - TS = H - TS = A + PV \]  
with total differential
\[ dG = -SdT + VdP \]  
The four functions, \(E, H, A,\) and \(G\) are known collec-
tively as thermodynamic potentials. General condi-
tions 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
line integrals we shall review briefly the theory of
(ordinary) (Riemann) integration for functions of a single
independent variable. The definite integral of a con-
tinuous function \(f(x)\) is defined by the limit:
\[ \int_a^b f(x)\,dx = \lim_{n \to \infty} \lim_{\Delta x_i \to 0} \sum_{i=1}^{n} f(x_i)\Delta x_i \]  
where \(\Delta x_i = x_i - x_{i-1}, x_0 = a,\) and \(x_n = b.\) The geom-
metrical 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
\[ \int_a^b f(x)\,dx = F(b) - F(a) \]  
where
\[ \frac{dF(x)}{dx} = f(x) \]  
This follows easily when the definition of the derivative
\[ \lim_{\Delta x_i \to 0} \frac{F(x_i) - F(x_{i-1})}{\Delta x_i} = f(x_i) \]  
is substituted into (80). We have then
\[ \sum_{i=1}^{n} |F(x_i) - F(x_{i-1})| = F(b) - F(a) \]  
which establishes (81). Also, using (82) in (81),
\[ \int_a^b dF(x) = F(b) - F(a) \]  
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)
\[ \Delta q = \int_{x',y'}^{x,y} [X(x,y)\,dx + Y(x,y)\,dy] = \]
\[ \lim_{n \to \infty} \lim_{\Delta x_i \to 0} \sum_{i=1}^{n} |X(x_i,y_i)\Delta x_i + Y(x_i,y_i)\Delta y_i| \]  
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

\[ x '' , y '' \]

\[ x', y', \Delta y_i, x_i, y_i, \Delta x_i \]

\[ C, C', x_i, y_i, \Delta x_i, \Delta y_i \]

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

Figure 3. The line integral, as defined in equation (86).
the line integral of force along a trajectory

\[ \Delta w = \int fF \cdot dr = \int fF_x dx + fF_y dy + fF_z dz \] (87)

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

\[ \int_C \int_{x', y'} dq(x, y) = -\int_C \int_{x', y'} dq(x, y) \] (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

\[ \Delta q_c = \int_{x'} X(x, y_0) dx \] (89)

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

\[ y = g(x) \] (90)
y can be eliminated between (86) and (90) to yield a Riemann integral

\[ \Delta q_c = \int_{x'} \left[ X[x, g(x)] + Y[x, g(x)] \frac{dy}{dx} \right] dx \] (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.](image)

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

\[ \Delta W = \int_{T_0 P_0}^{T_1 P_1} \left\{ \frac{RT}{P} \ dP - R \ dT \right\} \] (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:

\[ \Delta W_A = \int_{T_0 P_0}^{T_1 P_1} \left\{ \frac{RT}{P} \ dP - R \ dT \right\} + \int_{T_0 P_0}^{T_1 P_1} \left\{ \frac{RT}{P} \ dP - R \ dT \right\} = RT_1 \int_{P_0}^{P_1} \frac{dP}{P} - R(T_1 - T_0) \] (93)

Along path \( B \) we obtain analogously,

\[ \Delta W_B = RT_0 \ln \frac{P_1}{P_0} - R(T_1 - T_2) \] (94)

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

\[ T = \frac{T_0 + (T_1 - T_0)}{P_1 - P_0} \left( P - P_0 \right) \] (95)

whence

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

and

\[ dT = \frac{T_1 - T_0}{P_1 - P_0} \ dP \] (97)

Thus

\[ \Delta W_C = \int_{T_0 P_0}^{T_1 P_1} \left\{ \frac{RT}{P} \ dT - \frac{RT}{P_1} \ dP \right\} = RT_0 \ln \frac{P_1}{P_0} - RT_0 \frac{T_1 - T_0}{P_1 - P_0} \ln \frac{P_1}{P_0} \] (98)

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

\[ \Delta W_A \neq \Delta W_B \neq \Delta W_C. \] (99)

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

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

\[ \Delta V = \int_{T_0 P_0}^{T_1 P_1} \left\{ \frac{RT}{P} \ dT - \frac{RT}{P_1} \ dP \right\} \] (100)

along the same three paths, we find

\[ \Delta V_A = \Delta V_B = \Delta V_C = \frac{RT_1}{P_1} - \frac{RT_0}{P_0} = V_1 - V_0 \] (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

\[ \Delta F(x, y) = \Delta F(x, y) \Delta x + \Delta F(x, y) \Delta y \] (102)

where \( \Delta F(x, y) \) means \( F(x, y) - F(x_{-1}, y_{-1}) \). Substituting (102) in (86) we find

\[ \Delta q_c = \int_C \int_{x', y'} dq(x, y) = \lim_{n \to \infty} \sum_{i=1}^{n} \Delta F(x_i, y_i) = \Delta F(x, y) - F(x', y') \] (103)

independent of the path \( C \). Note the correspondance 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
sense. If \( dq(x,y) \) is an exact differential, then
\[
\oint_C dq(x,y) = \oint_C [X(x,y) dx + Y(x,y) dy] = 0 \tag{104}
\]
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
\[
\oint_C dq = \oint_{C'} dq + \oint_{C''} dq \tag{105}
\]
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:
\[
\oint_C [X(x,y) dx + Y(x,y) dy] = \iint_S \left[ \frac{\partial Y}{\partial x} - \frac{\partial X}{\partial y} \right] dx dy \tag{106}
\]
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
\[
dW = -pdV \tag{107}
\]
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
\[
\Delta W_C = -\oint_C pdV = -\iint_S dpdV \tag{108}
\]
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

\[\text{Figure 5. Line integral around closed path, as defined in equations (105) and (106).}\]

\[\text{Figure 6. Representation of work as area.}\]

\[
\Delta W_C = -\oint_{C_{P_0V_0}} pdV = -\int_{V_0}^{V_1} P(V) dV \tag{106}
\]
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
\[
dq(x,y) = X(x,y) dx + Y(x,y) dy \tag{109}
\]
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) \( c\oint dq(x,y) = 0 \) 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.

\[\text{The work done in traversing the path } C' \text{ from } P_0V_0 \text{ to } P_1V_1 \text{ is equal to the negative of the area under } C'.\]

\[
\Delta W_{C'} = -\oint_{P_0V_0} pdV \tag{109}
\]
The work done in returning to the original state via path \( C' \) is equal to the area under \( C' \).

\[
\Delta W_{C''} = -\oint_{P_0V_0} pdV = \oint_{P_1V_1} pdV \tag{109}
\]
The net work done in the cyclic process is given by
\[
\Delta W_C = \Delta W_{C'} + \Delta W_{C''} \tag{109}
\]
and is equal to the area enclosed by the cyclic path. The last result also follows from Green's theorem (106).