MATH BACKGROUND FOR THERMODYNAMICS

A. Partial Derivatives and Total Differentials

Partial Derivatives Given a function $f(x_1,x_2,...,x_m)$ of m independent variables, the partial derivative of f with respect to x_i, holding the other m-1 independent variables constant, $\left(\frac{\partial f}{\partial x_i}\right)_{x_{j\neq i}}$, is defined by

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_{j\neq i}} = \lim_{\Delta x_i \to 0}\left\{\frac{f(x_1,x_2,\ldots,x_i+\Delta x_i,\ldots,x_m)-f(x_1,x_2,\ldots,x_i,\ldots,x_m)}{\Delta x_i}\right\}$$

Example: If $p(n,V,T) = \frac{nRT}{V}$,

$$\left(\frac{\partial p}{\partial n}\right)_{V,T} = \frac{RT}{V} \qquad \left(\frac{\partial p}{\partial V}\right)_{n,T} = -\frac{nRT}{V^2} \qquad \left(\frac{\partial p}{\partial T}\right)_{n,V} = \frac{nR}{V}$$

Total Differentials Given a function $f(x_1,x_2,...,x_m)$ of m independent variables, the total differential of f, df, is defined by

$$df = \sum_{i=1}^{m}\left(\frac{\partial f}{\partial x_i}\right)_{x_{j\neq i}} dx_i$$

$$= \left(\frac{\partial f}{\partial x_1}\right)_{x_2,\ldots,x_m} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1,x_3,\ldots,x_m} dx_2 + \ldots + \left(\frac{\partial f}{\partial x_m}\right)_{x_1,\ldots,x_{m-1}} dx_m,$$

where dx_i is an infinitesimally small but arbitrary change in the variable x_i.

Example: For $p(n,V,T) = \frac{nRT}{V}$,

$$dp = \left(\frac{\partial p}{\partial n}\right)_{V,T} dn + \left(\frac{\partial p}{\partial V}\right)_{n,T} dV + \left(\frac{\partial p}{\partial T}\right)_{n,V} dT$$

$$= \frac{RT}{\mathrm{V}} dn - \frac{nRT}{V^2} dV + \frac{nR}{V} dT$$

B. Some Useful Properties of Partial Derivatives

1. The order of differentiation in mixed second derivatives is immaterial; e.g., for a function $f(x,y)$,

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y \quad \text{or} \quad \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

in the commonly used short-hand notation. (This relation can be shown to follow from the definition of partial derivatives.)

2. Given a function $f(x,y)$:

a. $\left(\frac{\partial y}{\partial f}\right)_x = \frac{1}{\left(\frac{\partial f}{\partial y}\right)_x}$ etc.

b. $\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial y}{\partial f}\right)_x \left(\frac{\partial x}{\partial y}\right)_f = -1$ (the cyclic rule)

Proof: The total differential of f is

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

We could, in principle, solve the equation $f = f(x,y)$ for y in terms of x and f; i.e., we could obtain the function $y(x,f)$. Its total differential would be given by

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

Substituting the above expression for df into the right-hand side of the expression for dy, we obtain

$$dy = \left(\frac{\partial y}{\partial x}\right)_f dx + \left(\frac{\partial y}{\partial f}\right)_x \left[\left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy\right]$$

or

$$0 = \left[\left(\frac{\partial y}{\partial f}\right)_x \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial y}{\partial x}\right)_f\right] dx + \left[\left(\frac{\partial y}{\partial f}\right)_x \left(\frac{\partial f}{\partial y}\right)_x - 1\right] dy \qquad \text{(I)}$$

Since dx and dy are arbitrary infinitesimal changes, the only way that the right-handside of (I) can be zero for all choices of dx and dy is if the coefficients of dx and dy are each separately equal to zero. Setting the coefficient of dy equal to zero gives

$$\left(\frac{\partial y}{\partial f}\right)_x \left(\frac{\partial f}{\partial y}\right)_x = 1 \quad \text{or} \quad \left(\frac{\partial y}{\partial f}\right)_x = \frac{1}{\left(\frac{\partial f}{\partial y}\right)_x} \qquad \text{q.e.d.}$$

Moreover, since any of the three variables *f*, *x*, and *y* could have been chosen as the dependent variable, it must also be true that

$$\left(\frac{\partial x}{\partial f}\right)_y = \frac{1}{\left(\frac{\partial f}{\partial x}\right)_y} \quad \text{and} \quad \left(\frac{\partial x}{\partial y}\right)_f = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_f}$$

Setting the coefficient of *dx* equal to zero in eqn. (I) gives

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

Thus,

$$\frac{\left(\frac{\partial y}{\partial f}\right)_x\left(\frac{\partial f}{\partial x}\right)_y}{\left(\frac{\partial y}{\partial x}\right)_f} = -1 \quad \text{or since} \quad \frac{1}{\left(\frac{\partial y}{\partial x}\right)_f} = \left(\frac{\partial x}{\partial y}\right)_f,$$

$$\left(\frac{\partial f}{\partial x}\right)_y\left(\frac{\partial y}{\partial f}\right)_x\left(\frac{\partial x}{\partial y}\right)_f = -1 \qquad \text{q.e.d.}$$

<u>Example</u>: Using the cyclic rule and the definitions $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$, show that $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\beta}$.

Solution: From the cyclic rule,

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

Thus,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p} = \frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{-V\alpha}{-V\beta} = \frac{\alpha}{\beta} \qquad \text{q.e.d.}$$

3. Given two functions of *x* and *y*: *f*(*x*,*y*) and *g*(*x*,*y*),

a. $\left(\frac{\partial f}{\partial g}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x\left(\frac{\partial y}{\partial g}\right)_x$ (chain rule)

b. $\left(\frac{\partial f}{\partial x}\right)_g = \left(\frac{\partial f}{\partial x}\right)_{\mathrm{y}} + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_g$

<u>Proof</u>: The total differential of *f* considered to be a function of *x* and *y* is

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

while the total differential of *y* considered to be a function of *x* and *g* is

$$dy = \left(\frac{\partial y}{\partial x}\right)_g dx + \left(\frac{\partial y}{\partial g}\right)_x dg.$$

Substituting this expression for *dy* into the expression for *df* above gives

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_g dx + \left(\frac{\partial y}{\partial g}\right)_x dg\right] \\ &= \left[\left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_g\right] dx + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial g}\right)_x dg. \end{aligned}$$

But if *f* is considered to be a function of *x* and *g*, rather than of *x* and *y*, its total differential is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_g dx + \left(\frac{\partial f}{\partial g}\right)_x dg.$$

These two expressions for *df* must be identical for any choice of the arbitrary infinitesimal changes *dx* and *dg*. Therefore, it must be true that

$$\left(\frac{\partial f}{\partial x}\right)_g = \left(\frac{\partial f}{\partial x}\right)_{\mathrm{y}} + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_g \quad \text{and} \quad \left(\frac{\partial f}{\partial g}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial g}\right)_x \quad \text{q.e.d.}$$

<u>*Examples*</u>:

1. For a van der Waals gas (i.e., a model system which obeys the van der Waals equation of state), the pressure *p* and the internal energy *U*, as functions of *n*, *V*, and *T*, are given by

   $$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad \text{and} \quad U = \tfrac{3}{2} nRT - \frac{n^2 a}{V}$$

   respectively, where a and b are constants. Use these equations and the chain rule to derive an equation for $\left(\frac{\partial U}{\partial p}\right)_{n,T}$ in terms of *n*, *V*, and *T*.

Solution: $\left(\frac{\partial U}{\partial p}\right)_{n,T} = \left(\frac{\partial U}{\partial V}\right)_{n,T}\left(\frac{\partial V}{\partial p}\right)_{n,T} = \frac{\left(\frac{\partial U}{\partial V}\right)_{n,T}}{\left(\frac{\partial p}{\partial V}\right)_{n,T}}$

$$= \frac{n^2 a / V^2}{\frac{2n^2 a}{V^3} - \frac{nRT}{(V-nb)^2}} = \frac{na}{\frac{2na}{V} - \frac{RTV^2}{(V-nb)^2}}$$

2. Given that the constant-volume heat capacity $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$, show that

$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \alpha V\left(\frac{\partial U}{\partial V}\right)_T$.

Solution: $\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$

But $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ and $\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$. Therefore,

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \alpha V\left(\frac{\partial U}{\partial V}\right)_T \qquad \text{q.e.d.}$$

Note: In this section, we have considered functions of two independent variables. However, all the relations derived hold for functions of more than two variables provided all the additional independent variables are held constant; e.g., for a function $f(w,x,y,z)$,

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_{w,x,z}\right]_{w,y,z} = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_{w,y,z}\right]_{w,x,z} \quad ,$$

$$\left(\frac{\partial f}{\partial x}\right)_{w,y,z}\left(\frac{\partial y}{\partial f}\right)_{w,x,z}\left(\frac{\partial x}{\partial y}\right)_{f,w,z} = -1, \quad \text{etc.}$$

C. Exact and Inexact Differentials; Line Integrals

Linear Differentials An infinitesimal quantity

$$dz = \sum_{\mathrm{i}=1}^{\mathrm{m}} M_{\mathrm{i}}(x_1, x_2, \ldots, x_{\mathrm{m}})dx_{\mathrm{i}}$$
$$= M_1 dx_1 + M_2 dx_2 + \ldots + M_{\mathrm{m}} dx_{\mathrm{m}}$$

is called a linear differential; the right-hand side of the equation is called a linear differential form in m variables. We shall be concerned primarily with linear differentials in two variables; in this case, let us write

$$dz = Mdx + Ndy$$

where M and N are, in general, functions of x and y.

Exact Differentials: $dz = Mdx + Ndy$ is an exact differential if and only if there exists a function of x and y, $F(x,y)$, such that $dF = dz$ for all values of x and y.

A more practically useful test for exactness is the following: $dz = Mdx + Ndy$ is an exact differential if and only if $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$.

It is easy to see that this relation must be true for an exact differential dz because in that case $M = \left(\frac{\partial F}{\partial x}\right)_y$ and $N = \left(\frac{\partial F}{\partial y}\right)_x$ and

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right]_y = \left(\frac{\partial N}{\partial x}\right)_y .$$

It can also be shown that the converse is true; i.e., if $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$, then dz is exact.

Inexact Differentials $dw = M'dx + N'dy$ is an inexact differential if and only if there exists no function $F(x,y)$, such that $dF = dw$ for all values of x and y. Equivalently, dw is inexact if and only if $\left(\frac{\partial M'}{\partial y}\right)_x \neq \left(\frac{\partial N'}{\partial x}\right)_y$.

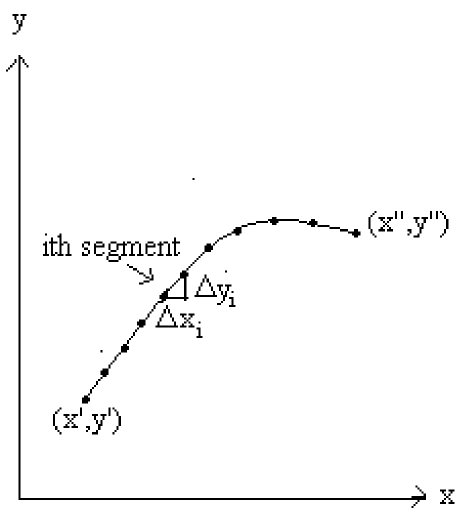
Examples: The linear differential $dz = xy^2dx + x^2ydy$ is an exact differential because it is the total differential of the function $F = ½\, x^2y^2 + \mathrm{C}$, where C is an arbitrary constant. Here,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(xy^2\right)\right]_x = 2xy = \left[\frac{\partial}{\partial x}\left(x^2y\right)\right]_y = \left(\frac{\partial N}{\partial x}\right)_y .$$

On the other hand, the linear differential $dw = x^2y\,dx + xy^2dy$ is inexact, as can most easily be demonstrated by noting that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(x^2y\right)\right]_x = x^2 \text{ while } \left(\frac{\partial N}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(xy^2\right)\right]_y = y^2$$

<u>Line Integrals</u> Consider a curve C in the X-Y plane connecting two points (x',y') and (x'',y'') and



imagine that we chop the curve up into n segments as shown at the left. Then the line integral I of the linear differential $dz = Mdx + Ndy$ on the curve C is defined by

$$I = \lim_{n\to\infty}\sum_{i=1}^{n}\left[M(x_i,y_i)\Delta x_i + N(x_i,y_i)\Delta y_i\right]$$

where $M(x,y)$ and $N(x,y)$ are given functions and $M(x_i,y_i)$ and $N(x_i, y_i)$ are the values of these functions at the midpoint of the ith segment. The notation we shall use for this integral is

$$I = \int_{\substack{(x',y') \\ C}}^{(x'',y'')}[Mdx + Ndy]$$

In order to carry out this integration, one must eliminate one of the variables x or y, which are related via the equation for the curve C, and then evaluate the resulting ordinary definite integral.

Examples:

1. Calculate the line integral of the inexact differential $dw = x^2ydx + xydy$ along the curve $y = x$ from (0,0) to (1,1).

   Solution: $I = \int_{\substack{(0,0) \\ y=x}}^{(1,1)}[x^2dx + xydy]$ But $y = x$ and $dy = dx$. Therefore,

$$I = 2\int_0^1 x^2dx = \tfrac{2}{3}x^3\Big|_0^1 = \tfrac{2}{3}$$

2. Calculate the line integral of $dw = x^2ydx + xydy$ along the curve $y = x^2$ from (0,0) to (1,1).

   Solution: $I = \int_{\substack{(0,0) \\ y=x^2}}^{(1,1)}[x^2dx + xydy]$ But $y = x^2$ and $dy = 2xdx$. Therefore,

$$I = \int_0^1 (x^2 + 2x^4)dx = \left(\tfrac{1}{3}x^3 + \tfrac{2}{5}x^5\right)\Big|_0^1 = \tfrac{1}{3} + \tfrac{2}{5} = \tfrac{11}{15}$$

Cyclic Integrals The cyclic integral $I = \oint_C dz$ is a line integral of the linear differential dz in which the path of integration is a closed curve; i.e., in which the initial and final points on C are the same.

Important Properties of Exact Differentials

1. If dz is an exact differential, then $\oint_C dz = 0$ for any closed curve C.

2. If dz is an exact differential, then $I = \int_{(x_1,y_1)\,C}^{(x_2,y_2)} dz$ is independent of the path C between the initial point (x_1,y_1) and the final point (x_2,y_2).

These properties are fairly obvious intuitively. Clearly, if dz is exact, it is the total differential of some function $F(x,y)$ and, therefore, $I = \int_{(x_1,y_1)\,C}^{(x_2,y_2)} dF = F(x_2,y_2) - F(x_1,y_1)$ independent of the path C. Furthermore, if $(x_2,y_2) = (x_1,y_1)$, then I is clearly equal to zero. Rigorous proofs of properties 1 and 2 are given at the end of this section for anyone interested. First, however, I'd like to preview the thermodynamic significance of exact and inexact differentials and line integrals.

Thermodynamic Significance As we shall see shortly, the properties of exact and inexact differentials and of line integrals are of very great importance in thermodynamics. For any infinitesimal thermodynamic transformation (change of state), the changes dp, dV, dU, dH, dS, dG, etc. in the various thermodynamic state functions are exact differentials, while the work done on the system dw and the heat absorbed by the system dq during the process are inexact differentials. For a finite thermodynamic transformation from state 1 to state 2, the change ΔF in any state function F is given by $\Delta F = F_2 - F_1$. On the other hand, q and w must be determined by evaluating line integrals whose value depends on the path of the transformation.

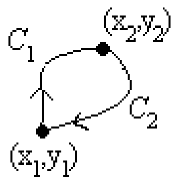
Proof of Property 1 It has been shown that the line integral of any linear differential around a closed curve C can be expressed in terms of a surface integral as follows:

$$\oint_C [Mdx + Ndy] = -\iint_A \left[\left(\frac{\partial M}{\partial y}\right)_x - \left(\frac{\partial N}{\partial x}\right)_y\right] dxdy \qquad \text{(Stokes' Theorem)}$$

where the integration on the right is over the area enclosed by the curve C. But $(\partial M/\partial y)_x = (\partial N/\partial x)_y$. since this is a necessary and sufficient condition for dz to be an exact differential. Hence,

$$\oint_C [Mdx + Ndy] = 0 \qquad \text{q.e.d.}$$

Proof of Property 2 Consider the closed curve C shown at the left. If dz is an exact differential,



$$0 = \oint_C dz = \int_{(x_1,y_1)\atop C_1}^{(x_2,y_2)} dz + \int_{(x_2,y_2)\atop C_2}^{(x_1,y_1)} dz$$

or

$$\int_{(x_1,y_1)\atop C_1}^{(x_2,y_2)} dz = -\int_{(x_2,y_2)\atop C_2}^{(x_1,y_1)} dz$$

As is true for any definite integral, if we interchange its limits of integration, the integral on the right will change sign; i.e.,

$$\int_{(x_2,y_2)\atop C_2}^{(x_1,y_1)} dz = -\int_{(x_1,y_1)\atop C_2}^{(x_2,y_2)} dz$$

Thus

$$\int_{(x_1,y_1)\atop C_1}^{(x_2,y_2)} dz = \int_{(x_1,y_1)\atop C_2}^{(x_2,y_2)} dz$$

But C_1 and C_2 could be any arbitrary curves connecting the points (x_1,y_1) and (x_2,y_2). Hence it must be true that $\int_{(x_1,y_1)\atop C}^{(x_2,y_2)} dz$ is independent of the path C.

q.e.d.

Exercises

1. Determine the total differential of each of the following functions:

   a. $z = e^{xy}$

   b. $z = \dfrac{1}{x+y}$

   c. $z = \ln(xy)$

   d. $z = x\sin y + y\sin x$

2. A useful equation of state for a real gas at low pressure and low temperature is the following:

$$p(V_m, \mathrm{T}) = \frac{RT}{V_m} - \frac{RTa}{V_m^{\,2}}$$

where V_m is the molar volume of the gas and a is a constant. Using this equation and the properties of partial derivatives, derive expressions for each of the following:

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

3. Given the functions $f(x,y) = x^2y + xy^2$ and $g(x,y) = e^{-(x^2+y^2)}$, derive expressions for the partial derivatives $\left(\frac{\partial f}{\partial g}\right)_x$ and $\left(\frac{\partial f}{\partial x}\right)_g$.

4. Determine whether or not each of the following linear differential forms is an exact differential.

a. $\dfrac{dx}{x^2y} + \dfrac{dy}{xy^2}$

b. $\dfrac{dx}{xy^2} + \dfrac{dy}{x^2y}$

c. $2x^2y\,dx + x^3dy$

d. $\ln y\,dx + \dfrac{x}{y}dy$

5. Evaluate each of the following line integrals:

a. $\displaystyle\int_{(1,1),\ y=x^2}^{(2,2)} \left[\frac{dx}{xy^2} + \frac{dy}{x^2y}\right]$

b. $\displaystyle\int_{(0,0),\ y=x}^{(1,1)} [x\sin y\,dx + y\sin x\,dy]$

c. $\displaystyle\oint_{C'} [x^3y\,dx + x^2y^2dy]$ over the triangular path C' shown at the right, which begins and ends at $(x,y) = (0,0)$.