THE CHEMIST'S TOOLKIT 10 Exact differentials

Suppose that $\mathrm{d}f$ can be expressed in the following way:

$$\mathrm{d}f = g(x,y)\mathrm{d}x + h(x,y)\mathrm{d}y \tag{10.1}$$

Is $\mathrm{d}f$ is an exact differential? If it is exact, then it can be expressed in the form

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \tag{10.2}$$

Comparing these two expressions gives

$$\left(\frac{\partial f}{\partial x}\right)_y = g(x,y) \quad \left(\frac{\partial f}{\partial y}\right)_x = h(x,y) \tag{10.3}$$

It is a property of partial derivatives that successive derivatives may be taken in any order:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y \tag{10.4}$$

Taking the partial derivative with respect to x of the first equation, and with respect to y of the second gives

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial g(x,y)}{\partial y}\right)_x$$
$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial h(x,y)}{\partial x}\right)_y \tag{10.5}$$

By the property of partial derivatives these two successive derivatives of f with respect to x and y must be the same, hence

$$\left(\frac{\partial g(x,y)}{\partial y}\right)_x = \left(\frac{\partial h(x,y)}{\partial x}\right)_y \tag{10.6}$$

If this equality is satisfied, then $\mathrm{d}f = g(x,y)\mathrm{d}x + h(x,y)\mathrm{d}y$ is an exact differential. Conversely, if it is known from other arguments that $\mathrm{d}f$ is exact, then this relation between the partial derivatives follows.

Brief illustration 10.1: Exact differentials

Suppose

$$\mathrm{d}f = \overbrace{3ax^2y}^{g(x,y)}\mathrm{d}x + \overbrace{(ax^3+2by)}^{h(x,y)}\mathrm{d}y$$

To test whether $\mathrm{d}f$ is exact, form

$$\left(\frac{\partial g}{\partial f}\right)_x = \left(\frac{\partial(3ax^2y)}{\partial y}\right)_x = 3ax^2$$

$$\left(\frac{\partial h}{\partial x}\right)_y = \left(\frac{\partial\left(ax^3+2by\right)}{\partial x}\right)_y = 3ax$$

The two second derivatives are the same, so $\mathrm{d}f$ is an exact differential and the function $f(x,y)$ can be constructed (see below).

Brief illustration 10.2: Inexact differentials

Suppose the following expression is encountered:

$$\mathrm{d}f = \overbrace{3ax^2y}^{g(x,y)}\mathrm{d}x + \overbrace{(ax^2+2by)}^{h(x,y)}\mathrm{d}y$$

(Note the presence of ax^2 rather than the ax^3 in the preceding *Brief illustration*.) To test whether this is an exact differential, form

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial(3ax^2y)}{\partial y}\right)_x = 3ax^2$$

$$\left(\frac{\partial h}{\partial x}\right)_y = \left(\frac{\partial(ax^2+2by)}{\partial x}\right)_y = 2ax$$

These two expressions are not equal, so this form of $\mathrm{d}f$ is not an exact differential and there is not a corresponding integrated function of the form $f(x,y)$.

Further information

If $\mathrm{d}f$ is exact, then

- From a knowledge of the functions g and h the function f can be constructed.
- It then follows that the integral of $\mathrm{d}f$ between specified limits is independent of the path between those limits.

The first conclusion is best demonstrated with a specific example.

Brief illustration 10.3: The reconstruction of an equation

Consider the differential $\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^3 + 2by)\mathrm{d}y$, which is known to be exact. Because $(\partial f/\partial x)_y = 3ax^2y$, it can be integrated with respect to x with y held constant, to obtain

$$f = \int \mathrm{d}f = \int 3ax^2y\,\mathrm{d}x = 3ay\int x^2\mathrm{d}x = ax^3y + k$$

where the 'constant' of integration k may depend on y (which has been treated as a constant in the integration), but not on x. To find $k(y)$, note that $(\partial f/\partial y)_x = ax^3 + 2by$, and therefore

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial(ax^3y+k)}{\partial y}\right)_x = ax^3 + \frac{\mathrm{d}k}{\mathrm{d}y} = ax^3 + 2by$$

Therefore

$$\frac{\mathrm{d}k}{\mathrm{d}y} = 2by$$

from which it follows that $k = by^2 + \text{constant}$. It follows that

$$f(x,y) = ax^3y + by^2 + \text{constant}$$

The value of the constant is pinned down by stating the boundary conditions; thus, if it is known that $f(0,0) = 0$, then the constant is zero.

To demonstrate that the integral of df is independent of the path is now straightforward. Because df is a differential, its integral between the limits a and b is

$$\int_a^b \mathrm{d}f = f(b) - f(a) \qquad (10.7)$$

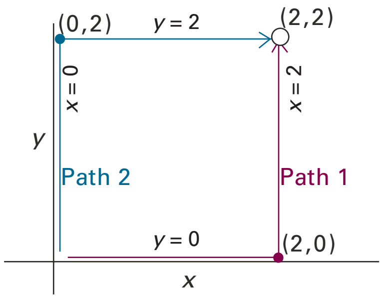
The value of the integral depends only on the values at the end points and is independent of the path between them. If df is not an exact differential, the function f does not exist, and this argument no longer holds. In such cases, the integral of df does depend on the path.

Brief illustration 10.4: Path-dependent integration

Consider the inexact differential (the expression with ax^2 in place of ax^3 inside the second parentheses):

$$\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^2 + 2by)\mathrm{d}y$$

Suppose df is integrated from (0,0) to (2,2) along the two paths shown in Sketch 10.1.



Sketch 10.1

Along Path 1,

$$\int_{\text{Path 1}} \mathrm{d}f = \int_{0,0}^{2,0} 3ax^2y\,\mathrm{d}x + \int_{2,0}^{2,2} (ax^2 + 2by)\mathrm{d}y$$
$$= 0 + 4a\int_0^2 \mathrm{d}y + 2b\int_0^2 y\,\mathrm{d}y = 8a + 4b$$

whereas along Path 2,

$$\int_{\text{Path 2}} \mathrm{d}f = \int_{0,2}^{2,2} 3ax^2y\,\mathrm{d}x + \int_{0,0}^{0,2} (ax^2 + 2by)\mathrm{d}y$$
$$= 6a\int_0^2 x^2\,\mathrm{d}x + 0 + 2b\int_0^2 y\,\mathrm{d}y = 16a + 4b$$

The two integrals are not the same.

An inexact differential may sometimes be converted into an exact differential by multiplication by a factor known as an *integrating factor*. A physical example is the integrating factor $1/T$ that converts the inexact differential $\mathrm{d}q_{\text{rev}}$ into the exact differential dS in thermodynamics (Topic 3B of the text).

Brief illustration 10.5: An integrating factor

The differential $\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^2 + 2by)\mathrm{d}y$ is inexact; the same is true when $b = 0$ and so for simplicity consider $\mathrm{d}f = 3ax^2y\mathrm{d}x + ax^2\mathrm{d}y$ instead. Multiplication of this df by x^my^n and writing $x^my^n\mathrm{d}f = \mathrm{d}f'$ gives

$$\mathrm{d}f' = \overbrace{3ax^{m+2}y^{n+1}}^{g(x,y)}\,\mathrm{d}x + \overbrace{ax^{m+2}y^n}^{h(x,y)}\,\mathrm{d}y$$

Now

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial(3ax^{m+2}y^{n+1})}{\partial y}\right)_x = 3a(n+1)x^{m+2}y^n$$

$$\left(\frac{\partial h}{\partial x}\right)_y = \left(\frac{\partial\left(ax^{m+2}y^n\right)}{\partial x}\right)_y = a(m+2)x^{m+1}y^n$$

For the new differential to be exact, these two partial derivatives must be equal, so write

$$3a(n + 1)x^{m+2}y^n = a(m + 2)x^{m+1}y^n$$

which simplifies to

$$3(n + 1)x = m + 2$$

The only solution that is independent of x is $n = -1$ and $m = -2$. It follows that

$$\mathrm{d}f' = 3a\mathrm{d}x + (a/y)\mathrm{d}y$$

is an exact differential. By the procedure already illustrated, its integrated form is $f'(x,y) = 3ax + a \ln y + \text{constant}$.