

CHEM1047 – Week 3 Lecture 2 – Partial derivatives

- Section 9.3 of Steiner, "The Chemistry Maths Book", 2nd edition.
- Section 4.5 of Cockett and Doggett, "Maths for Chemistry", Volume 1.

In physical sciences, functions rarely depend on just one variable. There are normally four variables associated with location in space and time, and further parameters pertaining to chemical systems, such as pressure, volume, temperature, concentrations, etc. Most derivatives encountered in the description of such systems are derivatives with respect to some variables, but not others.

1. Partial derivatives

A *partial derivative* of a function is a derivative with respect to just one of its arguments. The same differentiation rules apply, all other arguments should be treated as constants. Examples:

$$\frac{\partial}{\partial y}(xyz) = xz \qquad \frac{\partial}{\partial x}\left(\frac{1-x}{\sin y}\right) = \frac{-1}{\sin y}$$

Higher derivatives, such as $\partial^2 f / \partial x^2$, and mixed derivatives, such as $\partial^2 f / \partial x \partial y$, are obtained by sequential partial differentiation. For well-behaved functions, the value of mixed derivatives does not depend on the order of partial differentiation.

Partial derivatives have the same limit definition as the derivative of a univariate function:

$$\frac{\partial f(x, y, z, \dots)}{\partial x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x, y, z, \dots) - f(x, y, z, \dots)}{\Delta x} \quad (1)$$

The arguments are often collected into a vector for convenience, e.g.:

$$f(x, y, z) = f(\vec{r}), \quad \vec{r} = [x \quad y \quad z] \quad (2)$$

Example 1:

$$z = \sin(xy)$$

$$\frac{\partial z}{\partial x} = y \cos(xy) \qquad \frac{\partial z}{\partial y} = x \cos(xy) \qquad \frac{\partial^2 z}{\partial x^2} = -y^2 \sin(xy)$$

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial}{\partial y}[y \cos(xy)] = \cos(xy) - xy \sin(xy)$$

Example 2:

$$z = x^2 + y^2$$

$$\frac{\partial z}{\partial x} = 2x \qquad \frac{\partial z}{\partial y} = 2y \qquad \frac{\partial^2 z}{\partial x^2} = 2 \qquad \frac{\partial^2 z}{\partial x \partial y} = 0$$

2. Chain rules for multivariate functions

In situations when a function depends on multiple arguments that are themselves functions of other arguments, the *chain rule* for differentiation must be extended appropriately. Several situations exist:

1. A function of one variable that depends on multiple other variables:

$$\frac{\partial}{\partial x} f[g(x, y, z, \dots)] \quad (3)$$

We can use the definition of the derivative twice to write out Δf when the argument x is incremented by Δx , and then take the limit:

$$\Delta f = \frac{df}{dg} \Delta g + O[\Delta g^2] = \frac{df}{dg} \left(\frac{\partial g}{\partial x} \Delta x + O[\Delta x^2] \right) + O[\Delta g^2] \quad (4)$$

$$\frac{\partial f}{\partial x} = \lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \frac{df}{dg} \frac{\partial g}{\partial x}$$

We therefore arrive at the following chain rule:

$$\frac{\partial}{\partial x} f[g(x, y, z, \dots)] = \frac{df}{dg} \frac{\partial g}{\partial x} \quad (5)$$

2. A function of multiple variables that each depend on the same variable:

$$\frac{d}{dt} f[x(t), y(t), \dots] \quad (6)$$

This is a full derivative because the function ultimately only depends on one argument. Using the definition of a partial derivative followed by the definition of univariate derivative, we get:

$$\Delta f = \frac{\partial f}{\partial x} \Delta x + \frac{\partial f}{\partial y} \Delta y + \dots + O[\Delta x^2] + O[\Delta y^2] + \dots =$$

$$= \frac{\partial f}{\partial x} \frac{dx}{dt} \Delta t + \frac{\partial f}{\partial y} \frac{dy}{dt} \Delta t + \dots + O[\Delta x^2] + O[\Delta y^2] \quad (7)$$

After using the limit definition of the derivative with respect to t , we can conclude that:

$$\frac{d}{dt} f[x(t), y(t), \dots] = \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt} + \dots \quad (8)$$

3. A function of multiple variables that each depend on multiple other variables. This is a combination of the two situations above and the corresponding rule may be derived in a similar fashion:

$$\frac{\partial}{\partial \alpha} f[x(\alpha, \beta, \dots), y(\alpha, \beta, \dots), \dots] = \frac{\partial f}{\partial x} \frac{\partial x}{\partial \alpha} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial \alpha} + \dots \quad (9)$$

Example 3:

$$z = \sin(x), \quad x = u^2 v^2$$

$$\frac{\partial z}{\partial u} = \frac{dz}{dx} \frac{\partial x}{\partial u} = [\cos(x)][2uv^2] = 2uv^2 \cos(u^2 v^2)$$

Example 4:

$$z = x^2 y - y^2, \quad x = t^2, \quad y = 2t$$

$$\frac{dz}{dt} = \frac{\partial z}{\partial x} \frac{dx}{dt} + \frac{\partial z}{\partial y} \frac{dy}{dt} = [2xy][2t] + [x^2 - 2y][2] = \dots = 10t^4 - 8t$$

Example 5:

$$z = e^{x^2 y}, \quad x(u, v) = \sqrt{uv}, \quad y(u, v) = 1/v$$

$$\frac{\partial z}{\partial u} = \frac{\partial z}{\partial x} \frac{\partial x}{\partial u} + \frac{\partial z}{\partial y} \frac{\partial y}{\partial u} = [2xye^{x^2 y}] \left[\frac{\sqrt{v}}{2\sqrt{u}} \right] + [x^2 e^{x^2 y}][0] = \dots = e^u$$

3. Gradient vector

An important theorem in physics states that the force acting on a particle freely moving in some potential is equal to the partial derivatives of that potential:

$$E = U(x, y, z) \quad \Rightarrow \quad \vec{F} = \left[\frac{\partial U}{\partial x} \quad \frac{\partial U}{\partial y} \quad \frac{\partial U}{\partial z} \right] \quad (10)$$

Because force is a vector, it is often convenient to store all partial derivatives of a function in a vector as shown in Equation (10). Such a vector is called the *gradient* of the function:

$$\vec{\nabla} U = \left[\frac{\partial U}{\partial x} \quad \frac{\partial U}{\partial y} \quad \frac{\partial U}{\partial z} \quad \dots \right] \quad (11)$$

Gradient indicates the direction of steepest growth of the function and has many uses in physical sciences – for example, one of the best methods for decreasing the value of the function (called *gradient descent*) is to move in the direction opposite to its gradient.

4. Hessian matrix

Consider a weight of mass m attached to a spring of stiffness k and equilibrium length x_0 . From elementary mechanics we know that the total energy is the sum of kinetic and potential energies:

$$E = \frac{mv^2}{2} + \frac{k(x - x_0)^2}{2} \quad (12)$$

For a molecule with multiple atoms connected by multiple bonds, the expression is similar:

$$E = \frac{1}{2} \sum_n m_n |\vec{v}_n|^2 + \frac{1}{2} \sum_{n>m} k_{nm} \left(|\vec{r}_{nm}| - |\vec{r}_{nm}^{\text{eq}}| \right)^2 \quad (13)$$

where m_n is the mass of n -th atom, \vec{v}_n is its velocity vector, \vec{r}_{nm} is the distance vector between atom n and atom m , and the “eq” superscript refers to the equilibrium value. It is easy to see that the second derivatives of the energy with respect to the inter-atomic distances are the force constants:

$$\frac{\partial^2 E}{\partial |\vec{r}_{nm}|^2} = k_{nm} \quad (14)$$

This is very useful in practice because it allows vibrational frequencies to be calculated from derivatives of the total energy. The matrix of second derivatives of a function, for example:

$$\mathbf{H}[f(x, y)] = \begin{pmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} \end{pmatrix} \quad (15)$$

is called the *Hessian matrix*. It contains information about the local curvature of the function.