Partial derivatives in thermodynamics–
connections with MATH201

Let $f : \mathbb{R}^3 \longrightarrow \mathbb{R}$ be a given function, and consider the equation

$$f(x, y, z) = 0. \tag{1}$$

The implicit function theorem tells us when, given x and y, there is a unique z such that the equation holds. Such a value of z depends upon x, y so let us denote it by $q(x, y)$. Thus, for all appropriate (x, y) we have

$$f(x, y, q(x, y)) = 0. \tag{2}$$

Thus,

$$(x, y) \longmapsto q(x, y)$$

is a function of two variables. What are its partial derivatives? Differentiating (2) using the Chain rule gives

$$0 = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}0 + \frac{\partial f}{\partial z}\frac{\partial q}{\partial x} = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial z}\frac{\partial q}{\partial x}.$$

Thus,

$$\frac{\partial q}{\partial x} = -\frac{\dfrac{\partial f}{\partial x}}{\dfrac{\partial f}{\partial z}}. \tag{3}$$

Similarly, a function r of two variables may be defined by

$$f(r(y, z), y, z) = 0,$$

for appropriate (y, z). We find similarly to above that

$$\frac{\partial r}{\partial y} = -\frac{\dfrac{\partial f}{\partial y}}{\dfrac{\partial f}{\partial x}} \tag{4}$$

Also, a function s of two variables may be defined by

$$f(x, s(x, z), z) = 0,$$

for appropriate (x, z). We find similarly to above that

$$\frac{\partial s}{\partial z} = -\frac{\dfrac{\partial f}{\partial z}}{\dfrac{\partial f}{\partial y}} \tag{5}$$

We see from (3), (4) and (5) that

$$\frac{\partial q}{\partial x}\frac{\partial r}{\partial y}\frac{\partial s}{\partial z} = -1. \tag{6}$$

How do we interpret the above in the notation used in physical chemistry and physics, when thermodynamics is studied? In the above we have *named* the functions q, r, s obtained by expressing one variable in terms of the other two. The classical notation in physics does not distinguish between the functions so clearly, indicating the dependence on the different variables by using the existing symbols only and by use of subscripts. Thus, the partial derivative $\frac{\partial q}{\partial x}$ of the function q given in (2) above is denoted by

$$\left(\frac{\partial z}{\partial x}\right)_y.$$

Note that here the subscript of y does not denote partial differentiation—the idea is that $(\frac{\partial z}{\partial x})_y$ indicates that z is a function of x, y and that we are calculating the partial derivative of z with respect to x, keeping y fixed.

So, in thermodynamics

$$\frac{\partial q}{\partial x} \text{ is denoted by } \left(\frac{\partial z}{\partial x}\right)_y,$$

$$\frac{\partial r}{\partial y} \text{ is denoted by } \left(\frac{\partial x}{\partial y}\right)_z,$$

and

$$\frac{\partial s}{\partial z} \text{ is denoted by } \left(\frac{\partial y}{\partial z}\right)_x.$$

Thus, (6) becomes

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1. \tag{7}$$

This is symmetric in the 3 variables and (7) could be replaced by

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

for example, by interchanging the variables x and z.

Rod Nillsen, April 2006