Chapter 5

Relations between partial derivatives

5.1 Introduction

The importance of path and state functions, the relations between thermodynamic quantities and the use of (partial) differentials for thermodynamic issues is now clear. The next step is being able to determine a value or physical meaning for the partial derivatives so you can eventually find how much one quantity changes for a change in another quantity. Think of that bag of crisps, the manufacturer would really like to know by how much the volume increases if the pressure in the bag is increased and the temperature remains the same; for this, he needs to know the value of $(\frac{\partial V}{\partial P})_T$. Under the assumption that air behaves like an ideal gas, this is relatively simple to determine (see 2.3). However, most partial derivatives are much more difficult to determine; a number has been found in chapter 4. Eventually, all differentials can be determined. To this end, it is necessary to rewrite them into a different form so eventually one or more partial derivatives remain that are known (see chapter 8). When working with partial derivatives, a number of relations between the partial derivatives are useful. These relations are derived in this chapter.

5.2 Mixed derivatives

Equation 2.7 can also be expressed as

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y = M(x,y)\mathrm{d}x + N(x,y)\mathrm{d}y \tag{5.1}$$

in which

$$M = \left(\frac{\partial f}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial f}{\partial y}\right)_x . \tag{5.2}$$

Now, the partial derivative from M to y and the partial derivative from N to x can be taken. The result is a mixed derivative. In fact, a double derivative of f is taken here. First, there is differentiation to x and then to y or vice versa. This results in

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \frac{\partial^2 f}{\partial y \partial x} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \frac{\partial^2 f}{\partial x \partial y}. \tag{5.3}$$

Because quantities are continuous state functions (exact differentials), the order of differentiation does not matter (Clairaut's theorem, see Calculus) and the following applies:

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} \quad \text{and thus} \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y . \tag{5.4}$$

Relation 5.4 is a very important relation and can be used to check whether a differential df is exact or inexact (thus, whether it is a state or a path function, see chapter 3). If the differential is inexact, relation 5.4 does not apply. In thermodynamics, this relation is the basis for deriving the thermodynamic Maxwell relations. We will come back to the Maxwell relations in chapter 6.

5.3 The reciprocal rule and the cyclic rule

Now, two important relations for partial derivatives will be derived, **the reciprocal rule and the cyclic relation or -1 rule**. The function $f = f(x, y)$ can also be expressed as $x = x(f, y)$ if y and f are independent variables The total differential of $x = x(f, y)$ is

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \tag{5.5}$$

By combining the equations 5.1 and 5.5 and elimination of dx, the following is found

$$\mathrm{d}f = \left[\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f + \left(\frac{\partial f}{\partial y}\right)_x\right] \mathrm{d}y + \left(\frac{\partial x}{\partial f}\right)_y \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}f. \tag{5.6}$$

Rewriting the expression results in

$$\left[\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f + \left(\frac{\partial f}{\partial y}\right)_x\right] \mathrm{d}y = \left[1 - \left(\frac{\partial x}{\partial f}\right)_y \left(\frac{\partial f}{\partial x}\right)_y\right] \mathrm{d}f. \tag{5.7}$$

Because the variables y and f do not depend on each other, they can be varied independently from each other. For example, y can stay constant)$dy = 0$) while f can be varied around a large number of values ($df \neq 0$). For this reason, equation 5.7 can only be true if the terms between the square brackets are zero (regardless of the values of df and dy). Equalling the terms within the square brackets on the right-hand side to zero provides the reciprocal rule. This shows that the inverse of the partial derivative equals its reciprocal (or inverse) value

$$1 = \left(\frac{\partial x}{\partial f}\right)_y \left(\frac{\partial f}{\partial x}\right)_y \rightarrow \left(\frac{\partial x}{\partial f}\right)_y = \frac{1}{(\partial f/\partial x)_y}. \tag{5.8}$$

Equalling the terms within the square brackets on the left-hand side to zero provides the cyclic relation or -1 rule

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f = -\left(\frac{\partial f}{\partial y}\right)_x \rightarrow \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1. \tag{5.9}$$

5.4 Chain rule

Apart from the reciprocal rule and the cyclic rule, there is a third calculation rule that is called the **chain rule or dummy rule**. In a partial derivative a new, additional variable can be introduced and the partial differential can be spliced into two new partial derivatives.

$$\left(\frac{\partial x}{\partial f}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial f}\right)_y = \frac{\left(\frac{\partial x}{\partial w}\right)_y}{\left(\frac{\partial f}{\partial w}\right)_y}. \tag{5.10}$$

Note that for the chain rule, the subscripts are equal and that they differ in the -1 rule. Again, the mathematical relations between partial derivatives are summarised in table 5.1.

Reciprocal rule	$\left(\frac{\partial x}{\partial f}\right)_y = \frac{1}{(\partial f/\partial x)_y}$
Cyclic rule or -1 rule	$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1$
Chain rule or dummy rule	$\left(\frac{\partial x}{\partial f}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial f}\right)_y$

Table 5.1: *Overview of three mathematical relations for partial derivatives.*