Chapter 3

Path functions and state functions

3.1 Introduction

In order to see what the difference is between path and state functions (inexact and exact differentials), we will make quick trip back to the Alps. A hiker goes for a mountain hike and walks up the mountain. He performs work by walking up and the potential energy ($Epot = mgh$) of the hiker will increase during the hike. Once he arrives at the top, his potential energy has reached its maximum. The increase in potential energy can quite easily be calculated if the mass of the hiker and the height of the mountain are known. This potential energy increase will also be the same under all conditions. For other hikers, too, the potential energy is equal (if they are equally heavy). For example, it does not matter what the weather is like or how the hiker walked. So what about the work performed by the hiker? Is this the same in all cases, too? It will become clear that the work strongly depends on the path taken by the hiker; is he only going up or are there also declines and inclines along the route? If the hiker also has some declines, then in total he will probably have to perform more work to get to the top (of course, it is possible that the route with only inclines takes more work because it is a more difficult mountain track). The weather conditions will also affect the amount of work to be performed; if there is a pleasant temperature and not too much wind or if it rains then there will be less work required than if there is extreme cold, wind and snow.

When the hiker walks back down, his potential energy will decrease again. Back at the starting point of the hike, his potential energy is at the exact level it was when the hiker began his trip (assuming he has not become lighter or heavier). This, too, was set beforehand and the decrease again does not depend on the conditions. However, on the way back, the hiker performed work again. This performed work once again depends on the route the hiker followed and is not equal for everyone. It can be concluded that, after a day of hiking, the potential energy has not changed even though work has been performed. The potential energy only depends on the hiker's position and the work depends on the route followed and the conditions along the route.

Apparently there is a considerable difference between potential energy and work despite the fact that both are forms of energy; after all, they both have the dimension of energy, Joule (J). So what about other energy forms, such as heat transfer and enthalpy and quantities like pressure and temperature?

3.2 Path functions and state functions in thermodynamics

In thermodynamics, work and heat transfer are described by so-called **path functions**. This means that their value not only depends on the initial and final state, but also on the path (the route) that is followed to reach the result (figure 3.1). In order to, for example, go to a state of 100°C and 10 bar from a state of 25°C and 1 bar, it is possible to first heat up, then compress, or first compress and then heat up. All sorts of combinations are possible. The amount of work performed and the amount of heat that must be added will be different for all different options. Thus, the heat and work do not

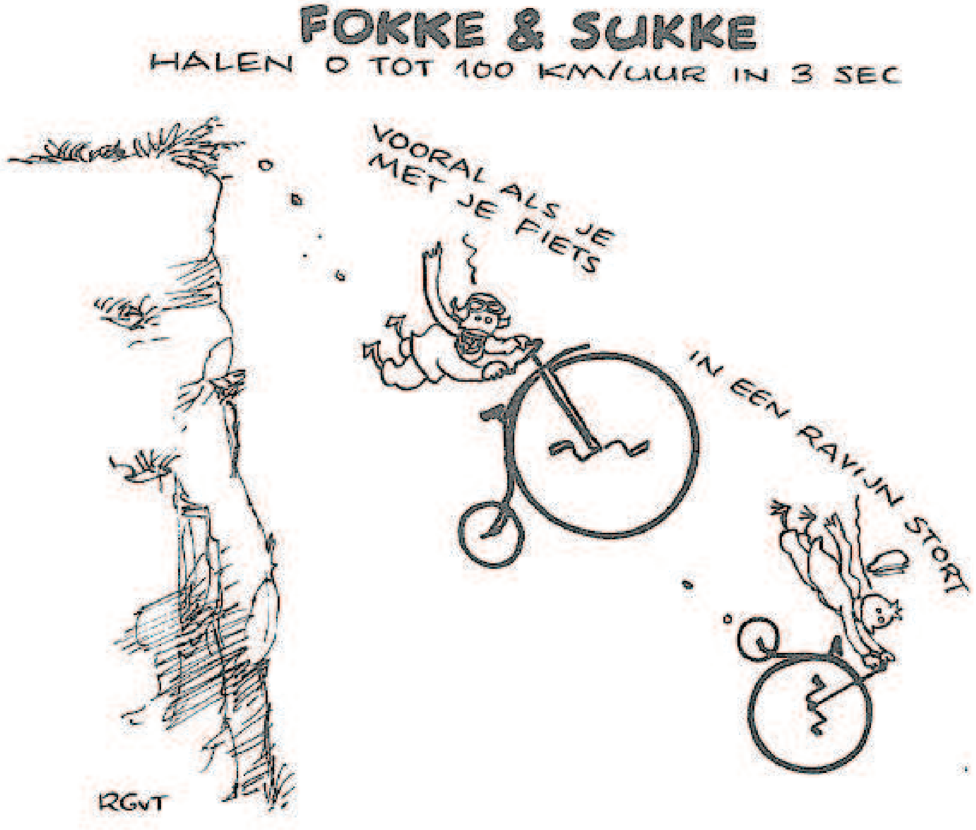

Figure 3.1: *The performed work depends on the route, work is an inexact differential; a path function (http://www.foksuk.nl/betacanon).*

depend on the properties of the state, but on the path that was followed to reach the state and are thus **path functions**.

Quantities, on the other hand, of which the value exclusively depends on the properties of the state in which it is in (regardless of the path taken to reach that state) are described by so-called **state functions**. Examples of this are: energy, enthalpy and entropy, but also quantities like pressure, volume and temperature. Also note that a state (i.e. a situation with a fixed temperature, pressure, energy, etc.) cannot perform work. Work can only be performed in a transition from one state to another state. In the case of the hiker, he will not have work on top of the mountain, but will have potential energy. He did, however, perform work to get from below the mountain, state 1, to on top of the mountain, state 2.

In order to indicate the difference between path functions and state functions, the differential difference in work and heat transfer is indicated by a δ, so δW and δQ, while changes in the state quantities are indicated by the standard symbol for the differential d, e.g. du, dh and dv.

Work and heat transfer, described by path functions, are known as **inexact** differentials while quantities of which the value is described by state functions are **exact** differentials. Instead of the terms exact and inexact differentials, the terms total and imperfect differential terms are used. The difference between inexact and exact differentials can be explained by means of mathematics.

3.3 Mathematics of exact and inexact differentials

In order to illustrate the difference between exact and inexact differentials, the differential of z

$$\delta z(x,y) = xydx + (x^2+2y)dy \tag{3.1}$$

is considered. First, this differential is integrated from state 1 at $z(1,1)$ to state 2 at $z(2,3)$ through state A at $z(1,3)$ around the path (1-A-2) indicated in figure 3.2a. The integral in this case will be

$$\begin{aligned}\int_{(1-A-2)} \delta z &= \int_{(1-A-2)} xydx + \int_{(1-A-2)} (x^2+2y)dy = \cancelto{0}{\left[\int_{y=1}^{y=3}(xy)dx\right]_{x=1,dx=0}} \\ &+ \left[\int_{y=1}^{y=3}(x^2+2y)dy\right]_{x=1,dx=0} + \left[\int_{x=1}^{x=2}(xy)dx\right]_{y=3,dy=0} + \cancelto{0}{\left[\int_{x=1}^{x=2}(x^2+2y)dy\right]_{y=3,dy=0}} \\ &= \int_1^3(1+2y)dy + \int_1^2(3x)dx = (y+y^2)\Big|_1^3 + \frac{3}{2}x^2\Big|_1^2 = (3+9-1-1)+(6-\frac{3}{2}) = 14.5.\end{aligned} \tag{3.2}$$

Now, the same function 3.1 is integrated around a different path: through state B at $z(2,1)$ as indicated in figure 3.2b. The integral for the function that is integrated around the path (1-B-2) will be

$$\int_{(1-B-2)} \delta z = \left[\int_{x=1}^{x=2} xydx\right]_{y=1,dy=0} + \left[\int_{y=1}^{y=3}(x^2+2y)dy\right]_{x=2,dx=0} = \int_1^2 xdx + \int_1^3 (4+2y)dy = 17.5. \tag{3.3}$$

Now it turns out that the outcome of both integrals is different. Despite the fact that the starting and end point of both paths is the same, the first path (1-A-2) results in a value of 14.5 and the second path (1-B-2) results in a value of 17.5. This means that the value of the integral depends on the path followed and thus δz is an inexact differential (path function).

The function 3.1 is now adjusted slightly by placing a 2 before the first term

$$dz(x,y) = 2xydx + (x^2+2y)dy. \tag{3.4}$$

Integration around the same two paths now results in

$$\Delta z = \int_{(1-A-2)} dz = \left[\int_{y=1}^{3}(1+2y)dy\right]_{x=1,dx=0} + \left[\int_{x=1}^{2}(6x)dx\right]_{y=3,dy=0} = 19 \tag{3.5}$$

and

$$\Delta z = \int_{(1-B-2)} dz = \left[\int_{x=1}^{x=2} 2xdx\right]_{y=1,dy=0} + \left[\int_{y=1}^{y=3}(4+2y)dy\right]_{x=2,dx=0} = 19. \tag{3.6}$$

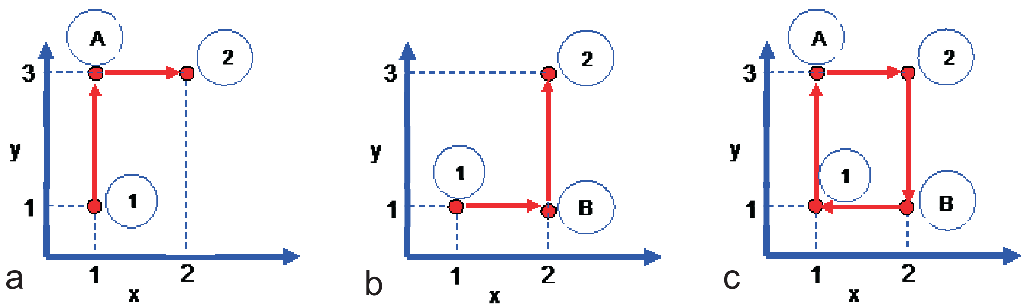

Figure 3.2: *a) Integration path from 1 to 2 through point A; b) Integration path from 1 to 2 through point B; c) Closed integration path (circle).*

The integral now results in the same value for both paths. All other parts will give 19 as a result of the integral. The integral's outcome is independent from the integration path. The new function dz from equation 3.4 is thus an exact differential (state function). An exact differential always has an integrated form from which the differential dz can be found. In the example, the function $z(x, y) = x^2y + y^2$ can be differentiated to find dz. However, there is no function $z(x, y)$ that results in δz after differentiation.

3.3.1 Contour integrals

An important property of an exact differential is that the outcome is 0 if the differential is integrated around a closed path, e.g. the path (1-A-2-B-1) as indicated in figure 3.2c. For an inexact differential, the outcome of the differentiation around a closed path will not result in 0. The integration around a closed path is called a circular integral and is indicated by the symbol $\oint$.

Integration around the closed path can be done for both differentials δz and dz. For δz of equation (3.1) this results in

$$\oint \delta z = \int_{(1-A-2)} \delta z + \int_{(2-B-1)} \delta z = 14.5 - 17.5 = -3.0 \tag{3.7}$$

and for dz from equation (3.4) the result is

$$\oint dz = \int_{(1-A-2)} dz + \int_{(2-B-1)} dz = 19 - 19 = 0. \tag{3.8}$$

Integration around a closed path for the path function/inexact differential (3.1) does not equal zero, while the integral around the closed path (always) results in zero for the state function/exact differential (3.4). For the example of the hiker, it is also clear that the work he performed during the hike described by a path function (inexact differential) is not zero, but that the change in potential energy described by a state function (exact differential) is zero. In conclusion, a differential is exact (state function) if the circular integral around a closed path is zero and if it does not matter which path is followed to go from one state to another. Chapter 5.2 discusses how you can check whether a differential is exact or inexact directly from the mathematical formula (without performing the integral).

3.4 Consequences of path and state functions in thermodynamics

What is the importance of all this in thermodynamics? Quantities such as pressure, temperature, volume, internal energy and enthalpy that fix a state have exact differentials (state functions) while work and heat have inexact differentials (path functions). *(Work and heat are not quantities!)*

There are many closed cycles in thermodynamics. A closed cycle is a series of processes in which the initial and final state are the same. Examples are the gas and steam cycles, but also the Otto and Diesel cycles for combustion engines and cooling cycles. In every closed cycle, the total integral around all states (circular integral) of a quantity (e.g. P, T, v, u and h) is zero. This is immediately clear by remembering that every state is described by a unique set of quantities (e.g. P, T, v, u and h). (Note that work and heat transfer do not describe a state; they are linked to a process between states.) If for a series of processes the initial and final state are the same, then the initial and final states of the various quantities will be the same and the change in each quantity will be zero and the contour integral will result in zero.

Work and heat transfer are inexact differentials and will generally result in a value not equalling zero when integrated around a closed cycle. This means that the net work and/or heat provided or requested in a closed cyclic process and their values depend on the path followed. Because work and heat are inexact differentials, a steam or gas cycle can provide work from heat that can be used to make electricity, for example.