

# Chapter 7

## Defined partial derivatives

### 7.1 Introduction

Apart from the partial quantities we have already discussed in chapter 4, there are a number of other partial derivatives that have a clear physical meaning and can be measured. These are the thermal expansion coefficient,  $\beta$ , and the isothermal compression coefficient,  $\kappa$  (see chapter 7.2). The specific heat at constant pressure is relatively easy to measure (see chapter 7.3). Furthermore, the change in pressure with the temperature at constant enthalpy plays an important part in throttling substances. This partial derivative  $(\partial P/\partial T)_h$  is called the Joule-Thomson coefficient (see chapter 7.4). All these quantities will be explained in this chapter.

### 7.2 Isothermal compression and thermal expansion

Only additional quantities are required for the description of specific thermodynamic processes. Go back to that bag of crisps from chapter 2. This concerned a change in volume as a result of a change in pressure and temperature. If  $v(T, P)$ , then the change in volume can be found by taking the total derivative of the volume. Consider that the volume is a thermodynamic quantity and, as such, is described by a state function and thus has an exact differential. The total differential of the volume is (see equation 2.8)

$$dv = \left(\frac{\partial v}{\partial P}\right)_T dP + \left(\frac{\partial v}{\partial T}\right)_P dT. \quad (7.1)$$

In section 2.3, this equation is calculated assuming the bag of crisps (the volume) was filled with an ideal gas. However, this is a more specific situation. It is useful to find a more general relation for the partial derivatives in the total differential of  $v$  from equation 7.1. To this end, the equation is divided by the volume

$$\frac{dv}{v} = \frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T dP + \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P dT. \quad (7.2)$$

The percentage change of the volume of a material for an isothermal change in pressure is called the *isothermal compression coefficient*,  $\kappa$ , , which is defined as

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T. \quad (7.3)$$

The minus symbol is required, because the partial derivative is always negative because a volume decreases when pressure increases. It is also important to know what the percentage change of the volume is for a temperature change in an isobaric process. This quantity is called the *thermal expansion coefficient* and is defined as

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P. \quad (7.4)$$

Both quantities can be measured relatively easily. When the quantities from the equations 7.3 and 7.4 are placed in 7.2 this results in

$$\frac{dv}{v} = \beta dT - \kappa dP. \quad (7.5)$$

Logically, the combination of  $P$ ,  $T$  and  $v$  leads to a third partial derivative, one in which  $v$  is constant. The quantity

$$\alpha = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_v \quad (7.6)$$

is called the *isochoric pressure coefficient*, called  $\alpha$  and indicates by which fraction the pressure will change if the temperature changes under a constant volume. However, this final quantity is generally difficult to measure. The isochoric pressure coefficient can be expressed in  $\beta$  and  $\kappa$ .

### 7.3 Specific heat

If a specific amount of heat (energy) is added to a block of iron, the temperature will increase. The proportionality constant between the amount of energy and the temperature increase of the block of iron is called the specific heat (or heat capacity). Roughly, you can say that the specific heat of the change in energy is divided by the change in temperature

$$C = \frac{\Delta \text{Energy}}{\Delta T}. \quad (7.7)$$

This is an approximation, however; there are different types of specific heat depending on the process the system goes through. This way, the volume or the pressure can remain constant during heating. When a balloon is heated, it will expand and the pressure will remain constant. However, during the heating of a rigid ball, the volume will not be able to expand and the pressure inside the ball will increase. The first process, heating at a constant pressure requires more energy. After all, volume work must be performed as well. That is why there is a distinction between different specific heat coefficients. The specific heat for a constant-volume process,  $c_v$  is defined as the change in internal energy as a result of the change in temperature

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v = T \left( \frac{\partial s}{\partial T} \right)_v. \quad (7.8)$$

Similarly, the specific heat for a constant-pressure process,  $c_p$  is defined as the change in enthalpy as a result of the change in temperature

$$c_p = \left( \frac{\partial h}{\partial T} \right)_P = T \left( \frac{\partial s}{\partial T} \right)_P. \quad (7.9)$$

Consider that the specific heat for a process at a constant pressure is always greater than the specific heat for a process at a constant volume, because the system can expand at a constant pressure and the required energy must also be added (for expansion, volume work,  $\delta w = P dv$ , is performed). Note that for the *specific* heat (or *specific* heat capacity) a lower case letter  $c$  is used. As you will remember, specific means that it is the amount of heat that needs to be added per kg of material. The unit of  $c$  is J/kgK. A capital letter  $C$  is used for the total specific heat (or the total heat capacity) of the material,  $C = mc$ , with J/K as the unit.

Thus, there is an isobaric specific heat coefficient and an isochoric specific heat coefficient. The former is relatively easy to measure, the latter proves more difficult. The quantities  $c_P$  and  $c_v$  are related through the Nernst-Lindeman relation,

$$c_v = c_P - \frac{T v \beta^2}{\kappa}. \quad (7.10)$$

## 7.4 The Joule-Thomson coefficient

In physics, the Joule-Thomson effect is a description of the temperature change of a gas or fluid that is forced through a valve or porous plug without exchanging heat with the surroundings. This is commonly done through a thermal expansion valve or a Joule-Thomson valve. In this process, which is called throttling, the substance encounters resistance and the pressure decreases<sup>1</sup> (the resistance can be a narrowing of a pipe or a valve as shown in figure 7.1a). In a throttling process, the enthalpy,  $h$ , is constant. The question now is what happens to the temperature? In many cases, the temperature will strongly decrease in a throttling process. In, for example, a refrigerator or air conditioner, throttling is the process that ensures the temperature decreases. In throttling, the temperature will not always decrease, however; it can also increase or remain constant. The behaviour of the temperature as a result of the pressure change during a throttling process ( $h$  is constant) can be described with the help of a partial derivative. This is called the **Joule-Thomson coefficient**. The partial derivative gives the change in temperature as a result of a change in pressure at a constant enthalpy and is defined as

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_h. \quad (7.11)$$

The Joule-Thomson coefficient is a measure for the change in temperature as a result of the change in pressure at a constant enthalpy (isenthalpic) process. If  $\mu_{JT} = 0$ , then the temperature is constant, if  $\mu_{JT} < 0$  (negative), then the temperature increases and if  $\mu_{JT} > 0$  (positive), then the temperature decreases during the throttling process for which the enthalpy is constant.

Graphically, the Joule-Thomson coefficient represents the incline of the lines with a constant enthalpy (isenthalps) in a  $PT$  diagram, such as in figure 7.1b. Such diagrams can be easily made by measuring the temperature and pressure during a throttling process.

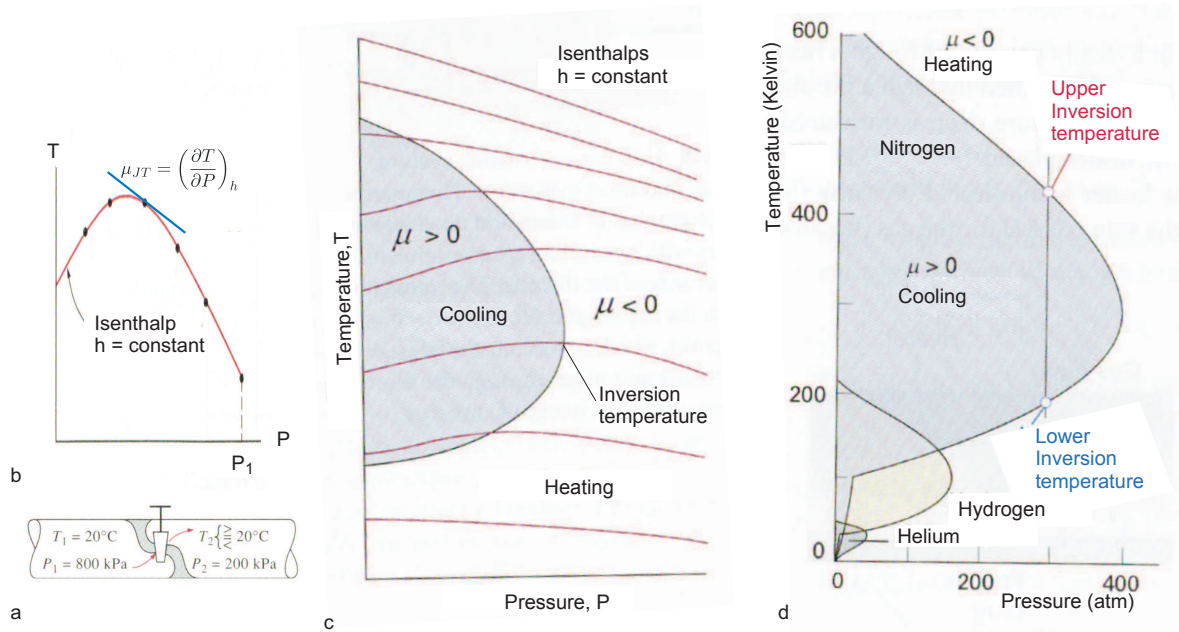


Figure 7.1: a) Throttling process, the temperature of the substance can increase, decrease or remain constant at expansion. b)  $PT$  diagram, the Joule-Thomson coefficient is the tangent with the line of constant enthalpy. c) The curve with the inversion temperature intersects with the isenthalps at their maximum, the incline is negative within the curve (hatched area), the gas is cooled, outside of the area, the incline is positive, the gas heats upon expansion. d) The inversion temperature for a number of real gases.

<sup>1</sup>This follows from Bernoulli's equation:  $P + \frac{1}{2}\rho v^2 + \rho g z = \text{constant}$ .

The isenthalps in the  $PT$  diagram often have a maximum. At the maximum, the Joule-Thomson coefficient equals zero and the temperature of the gas will not change during the throttling process. To the left of the maximum, the incline of the isenthalp is positive and the temperature will decrease during throttling. To the right of the maximum, the incline is negative and the temperature will increase during throttling. This is represented graphically in figure 7.1c.

The temperature at the maximum, above which the temperature will increase upon expansion with constant enthalpy, and below which the temperature decreases as a result of the expansion, is called the inversion temperature. The inversion temperature depends on the pressure. At atmospheric pressure, the inversion temperature for most real gases is above room temperature. This means that most gases can be cooled in a throttling process. Exceptions to this are hydrogen, helium and neon. These gases have a (very) low inversion temperature at atmospheric pressure (hydrogen:  $-71^{\circ}\text{C}$  (202 K), helium:  $-233^{\circ}\text{C}$  (40 K), neon:  $-42^{\circ}\text{C}$  (231 K)) and heat up if they are expanded adiabatically at atmospheric pressure. Nitrogen and oxygen, the two most common gases in air have respective inversion temperatures of  $348^{\circ}\text{C}$  (621 K) en  $491^{\circ}\text{C}$  (764 K). The inversion temperature of air lies below this with  $330^{\circ}\text{C}$  (603 K). In figure 7.1d, the inversion curve for helium, hydrogen and nitrogen have been provided. Gases with an inversion temperature exceeding room temperature can be 'easily' cooled by the Joule-Thomson effect. This process is applied, among other things, for liquidizing gas.

For an ideal gas, the Joule-Thomson coefficient always equals zero. This means that an ideal gas cannot be cooled nor heated upon expansion.

The Joule-Thomson effect is caused by two opposing physical phenomena. When a gas expands (decrease in pressure), the mean distance between the molecules increases. As a result of the van der Waals forces, the expansion causes an increase in the gas' potential energy. If no work is performed and no heat is transported, the total amount of energy will remain equal as a result of the law of conservation of energy. The increase of potential energy thus causes a decrease of kinetic energy and, therefore, a decrease in temperature.

A second phenomenon that occurs at the same time has the opposite effect, however. When molecules collide, kinetic energy is temporarily converted into potential energy. Because the mean distance between the molecules has increased, the number of collisions per time unit decreases, which means that the average potential energy decreases. Due to the law of conservation of energy, this leads to an increase of the kinetic energy (temperature). Under the influence of the Joule-Thomson inversion temperature, the first effect predominates and free expansion causes a decrease in temperature. Above the inversion temperature the molecules move faster and there are more collisions, and the second effect predominates: Joule-Thomson expansion causes an increase in temperature.

The effect was named after James Prescott Joule and William Thomson (better known as Lord Kelvin). The latter discovered the effect in 1852 as a result of prior work by Joule regarding gas expansion in a vacuum.