Thermodynamics Summary

1. Thermodynamics Definitions

1.1   Introduction to Thermodynamics

Thermodynamics is the science of energy. There are two kinds of thermodynamics. When applying **classical thermodynamics**, we do not consider individual atoms. We only look at a so-called **continuum**. In **statistical thermodynamics** we do deal with large groups of particles. In this summary we will generally discuss classical thermodynamics though.

1.2   Systems and their Properties

A **system** is defined as a quantity of matter or a region in space chosen for study. The mass/region outside the system is called the **surroundings**. The surface in between is the **boundary**. The boundary can be fixed or movable. A system can also be closed or open. In a **closed system** no mass can cross the boundary, while in an **open system** (also called a **control volume**) mass exchange with the surroundings is possible.

A characteristic of a system is called a **property**. There are multiple types of properties. **Intensive properties** do not directly depend on the amount of matter in the system (like temperature and pressure). **Extensive properties** like mass and volume do directly depend on the number of particles. When extensive properties are calculated per unit mass, then they are **specific properties**. These specific properties are usually denoted by small letters. Examples are the **specific volume** $v = \rho^{-1}$ (where ρ is the density) and the **specific weight** $\gamma = \rho g$.

1.3   Equilibrium States

In thermodynamics, we consider the **state** or condition of a system. We usually deal with **equilibrium states**. A system in equilibrium experiences no changes when it is isolated from its surroundings. A system is in **thermal equilibrium** if the temperature is the same throughout the system. It is in **mechanical equilibrium** if the pressure stays constant. There are also more complicated types of equilibrium. Only if all the above equilibrium states are present, a system is in so-called **thermodynamic equilibrium**.

But how do we express the state of a system? We do this by using properties. The **state postulate** says that the state of a simple compressible system is specified by two independent intensive properties. This postulate requires some clarification. A system is **compressible** if the density isn't constant throughout the system. A system is a **simple system** if electrical effects, magnetic effects, gravitational effects, and so on, are not present. (Otherwise an additional property is needed for every effect that is present.) Also two properties are **independent** if one property can be varied while the other is held constant.

1.4   Processes

A **process** is the change of a system from one state to another. The **path** is the series of states through which the system passes. A system has undergone a **cycle** if the initial and final states of the process are

the same.

There are multiple types of processes. When the system remains very close to an equilibrium state at all times, we have a **quasi-static process**. In a **steady-state flow process** a fluid flows through a control volume steadily. The term **steady** indicates nothing changes in time.

Also the prefix "iso" can be used to indicate certain properties stay constant. In an **isothermal process** the temperature T stays constant. In an **isobaric process** the pressure P remains the same. Finally in **adiabatic processes** there is no heat exchange with the surroundings.

1.5 Pressure

Pressure is a normal force exerted per unit area. It is the same in all directions, and is therefore a scalar quantity. The **absolute pressure** is the pressure measured relative to a vacuum. Pressure is often measured with respect to atmospheric pressure. We then speak of **gage pressure**. In thermodynamics, the absolute pressure (denoted by P) is almost always used though.

The pressure varies with the height z, due to gravity. How this occurs can be derived by looking at a small piece of fluid/gas. Doing this will result in

$$\frac{dP}{dz} = -\rho g = -\gamma. \tag{1.5.1}$$

This principle is used in a **manometer**. This is a device that measures pressure differences. It consists of a U-tube with a fluid, connecting two parts A and B. When a pressure difference is present between A and B, then the fluid levels h_A and h_B will not be equal. The relation between the pressures in A and B is then given by

$$P_A - P_B = \rho g \left(h_B - h_A \right) = \gamma \left(h_B - h_A \right). \tag{1.5.2}$$

2. Energy

2.1 Introduction to Energy

One of the most fundamental laws of nature is the **conservation of energy principle**. In fact, this is the first law of thermodynamics. Energy can not be created or destroyed. It can only change form. But what is energy? That's what we'll look at in this chapter.

There are multiple types of energy (think of kinetic energy, potential energy, thermal energy, and so on). The sum of all these energy types forms the **total energy** E. The total energy per unit mass is $e = E/m$ (with m the mass of the system).

All energy types can be split up in two groups, being the macroscopic types and the microscopic types. **Macroscopic** forms of energy depend on the reference frame. Examples are kinetic energy and potential energy. **Microscopic** forms of energy are related to the molecular structure of a system. The sum of all microscopic forms of energy in a system is called the **internal energy** U.

2.2 Macroscopic Energy

Let's take a closer look at the macroscopic forms of energy. We already mentioned **kinetic energy**. Its magnitude for a particle moving with velocity ν can be found using

$$KE = \frac{1}{2}m\nu^2, \qquad ke = \frac{1}{2}\nu^2. \tag{2.2.1}$$

Note that, next to the total kinetic energy KE, we have also mentioned the kinetic energy per unit mass ke. The **potential energy** due to a gravitational field can be found using

$$PE = mgz, \qquad pe = gz. \tag{2.2.2}$$

If we ignore other more complicated types of energy (like electrical energy, magnetic energy, etcetera), we can find the total energy to be

$$E = U + KE + PE = U + \frac{1}{2}m\nu^2 + mgz, \qquad e = u + ke + pe = u + \frac{1}{2}\nu^2 + gz. \tag{2.2.3}$$

2.3 Microscopic Energy

Now let's take a closer look at the microscopic forms of energy. To do that, we have to look at the molecules of a substance. These molecules move. The kinetic energy associated with this is the **sensible energy**.

Internal forces act between molecules. If sufficient energy is added, these internal forces are overcome. This may cause the substance to change its phase (for example from liquid to gas). When the phase changes back, energy is released again. This energy, related to the phase, is called the **latent energy**.

In real life, we usually refer to sensible and latent energy as heat. However, in thermodynamics we use the term **thermal energy** (to prevent confusion).

Finally there are also **chemical energy**, associated with bonds within a molecule, and **nuclear energy**, associated with the nucleus of the atom itself. Although the magnitude of these energies can be big, they are generally hard to access.

2.4 Energy Transfer

Energy can be transferred between systems in multiple ways. **Heat** is the form of energy that is transferred between systems due to a temperature difference. If there is no heat transfer in a process, then the process is an **adiabatic process**. Heat can be transferred by three mechanisms. In **conduction** the transfer occurs due to interaction between adjacent particles. **Convection** is the heat transfer between a solid surface and an adjacent moving fluid. Finally **radiation** is the transfer of energy due to the emission of electromagnetic waves.

The **work** W is the energy transfer caused by a force acting through a distance. Work done per unit time is called **power**. Usually the amount of work performed can be calculated using

$$W = \int_1^2 F \, ds, \tag{2.4.1}$$

where s is the distance moved. But sometimes there isn't a clear force. When a shaft is rotating, due to a torque T, the amount of work done is equal to

$$W_{shaft} = \int_1^2 T \, d\phi, \tag{2.4.2}$$

where ϕ is the angle over which the shaft is rotated. Another example is a spring. Here the force depends on the displacement, according to $F = kx$. So now we have as work done

$$W_{spring} = \int_1^2 kx \, dx = \frac{1}{2} k \left(x_2^2 - x_1^2 \right). \tag{2.4.3}$$

The last way in which energy can be transferred is by a mass flow. Let's consider the case where an amount of mass enters the system. This mass has internal energy. Therefore the total energy of the system rises. Identically, when mass is removed, the total energy decreases.

2.5 Mechanical Energy

Mechanical energy is the form of energy that can be converted to work completely. While kinetic and potential energy are types of mechanical energy, thermal energy is not.

Now let's consider pressure. Pressure itself isn't an energy. But it can produce work, called **flow work**. The magnitude of flow work (per unit mass) can be found using P/ρ. The mechanical energy per unit mass therefore becomes

$$e_{mech} = \frac{P}{\rho} + \frac{1}{2} \nu^2 + gz. \tag{2.5.1}$$

2.6 Performance

The **efficiency** of a system is defined as

$$\eta = \text{efficiency} = \frac{\text{Desired output}}{\text{Required input}} = 1 - \frac{\text{Loss}}{\text{Required input}}. \tag{2.6.1}$$

We can think of awfully many types of efficiencies. Examples are the **combustion efficiency** and the **mechanical efficiency**. These are defined as

$$\eta_{combustion} = \frac{\text{Heat released during combustion}}{\text{Heating value of the fuel burned}}, \qquad \eta_{mechanical} = \frac{\text{Mechanical energy output}}{\text{Mechanical energy input}}. \tag{2.6.2}$$

Sometimes multiple efficiencies need to be combined (multiplied) to find the **overall efficiency** of a system. This efficiency is an indication of how well the system performs its job.

3. Pure Substances

3.1 Introduction to Pure Substances

A **pure substance** is a substance that has a fixed chemical composition. This can be a mixture of elements, as long as the mixture is homogeneous.

Pure substances can come in various phases. In a **solid**, the molecules are arranged in a three-dimensional pattern (the lattice) that repeats through the material. In a **liquid** the molecules can move and rotate freely, but are still quite close together. Finally, in a **gas**, the molecules are far apart from each other.

When dealing with pure substances, often the quantity $u + Pv$ is encountered. This quantity has therefore been given its own name. The **enthalpy** h is thus defined as

$$h = u + Pv. \tag{3.1.1}$$

3.2 Vaporizing a Liquid

Let's suppose we want to vaporize a liquid to its gas form. Initially the liquid is not about to vaporize. We say it is a **compressed liquid** or a **subcooled liquid**. We then add heat. After a while, the liquid will be about to vaporize. We now call it a **saturated liquid**. When part of the liquid has vaporized, and part has not, we have a **saturated liquid-vapor mixture**. Finally, when all the liquid has vaporized and we only have vapor left, we have a **saturated vapor**. This vapor it still about to condense. If we heat it further, then it won't be about to condense any more. We are then dealing with a **superheated vapor**. The heat which is absorbed to make the phase change is called the **latent heat**.

At a given pressure, the temperature at which pure substances change phase is called the **saturation temperature** T_{sat}. Identically, for a given temperature, the pressure at which the phase changes is called **saturation pressure** P_{sat}. A plot of these two is called a **liquid-vapor saturation curve**. Such a plot is shown in figure 3.1.
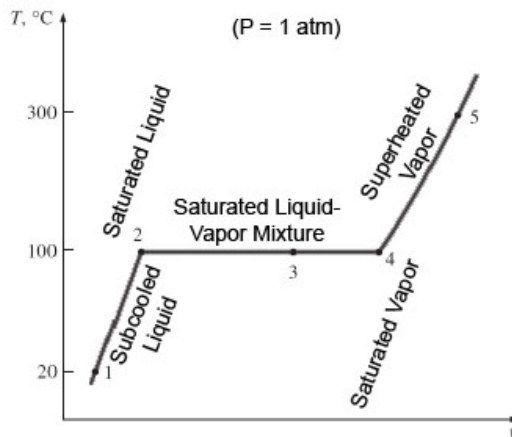

Figure 3.1: The liquid vapor saturation curve for water.

3.3 Mixture Quality

When the liquid is saturated, it has a certain specific volume v_f. Identically, the saturated vapor has a specific volume v_g. The change in specific volume v_{fg} is then defined as $v_{fg} = v_g - v_f$. Identically the **enthalpy of vaporization** (or **latent heat of vaporizaton**) is defined as $h_{fg} = h_g - h_f$. In the critical point, which will be discussed soon, both v_{fg} and h_{fg} are zero.

During vaporization there will be a mixture of liquid and vapor. The **quality** x of this mixture (having a value between 0 and 1) is defined as

$$x = \frac{m_{vapor}}{m_{total}}. \tag{3.3.1}$$

The **average specific volume** of the mixture can be found using

$$v_{avg} = \frac{m_{liquid}v_f + m_{vapor}v_g}{m_{total}}. \tag{3.3.2}$$

Now the quality of the mixture can also be calculated using

$$x = \frac{v_{avg} - v_f}{v_{fg}}. \tag{3.3.3}$$

Usually v_f and v_{fg} are known for a substance. Only the average specific volume then needs to be measured to find the quality of the mixture. And once the quality is known, the average internal energy u_{avg} and the average enthalpy h_{avg} can be found using

$$u_{avg} = u_f + xu_{fg}, \qquad \text{and} \qquad h_{avg} = h_f + xh_{fg}. \tag{3.3.4}$$

3.4 $T - v$ Diagrams

The variations of properties during phase-change processes are best studied and understood with the help of **property diagrams**. There are $T - v$, $P - v$ and $P - T$ diagrams. First let's consider $T - v$ diagrams.

The $T - v$ diagram for water is shown in figure 3.2. When vaporizing water at low pressures, there still is a region in which a saturated liquid-vapor is present. This region is called the **saturated liquid-vapor region**. To the left of this region is a **subcooled liquid region** and to the right is a **superheated vapor region**.
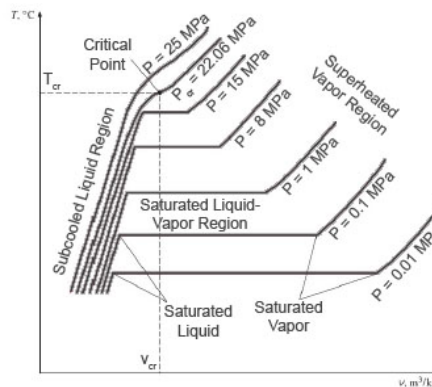

Figure 3.2: Diagram plotting the temperature versus the specific volume.

There are many saturated liquid points now. The line connecting these points is called the **saturated liquid line**. This line separates the subcooled liquid region from the saturated liquid-vapor region. The

line connecting the saturated vapor points is called the **saturated vapor line**. The point where these two lines meet is the **critical point**. Corresponding to this point are the **critical temperature** T_{cr}, the **critical pressure** P_{cr} and the **critical specific volume** v_{cr}.

The $P - v$ diagram is very similar to the $T - v$ diagram. But although the v increases with increasing T, the specific volume v decreases for increasing P. So while the lines in figure 3.2 go upward, in a $P - v$ diagram they go downward.

3.5 $P - T$ **Diagrams**

Given the pressure and temperature of a substance, its phase can be derived. This is done using $P - T$ diagrams. Such a diagram is shown in figure 3.3.
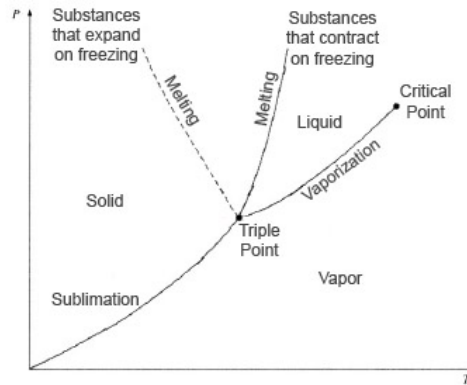

Figure 3.3: Diagram showing the phase of a pure substance, given its pressure and temperature.

So we see that at low pressures it is possible for a solid to change to a gas without becoming liquid. Also, at high pressures (higher than the critical pressure), a liquid can turn to a gas without any clear transition. But maybe the most interesting point in figure 3.3 is the **triple point**. This is the point where all three phases can coexist in equilibrium.

Now we have discussed $T - v$, $P - v$ and $P - T$ diagrams. However, there are also $P - v - T$ diagrams. These are three-dimensional diagrams, consisting of a so-called $P - v - T$ **surface**. Using this surface, it is usually possible to determine one of the three properties, once the other two are known.

3.6   **Property Equations**

It's nice to have graphs showing the relation between properties. But sometimes it's more convenient to have an equation that does the same thing. Any equation that relates the pressure, temperature and specific volume of a substance is called an **equation of state**. The problem is that there is no equation of state that always works.

The most well-known equation of state is the **ideal-gas equation of state** (or **ideal-gas relation**), stating that

$$Pv = RT. \tag{3.6.1}$$

Here R is the **gas constant**, which differs per gas. For high specific volume gases this equation is rather accurate. However, as the state of the gas becomes closer to the saturated vapor line, this equation loses its accuracy.

This equation can be made more accurate, using the **compressibility factor** Z, defined as

$$Z = \frac{Pv}{RT}.\tag{3.6.2}$$

Let's also define the **reduced pressure** P_R and the **reduced temperature** T_R as

$$P_R = \frac{P}{P_{cr}} \qquad \text{and} \qquad T_R = \frac{T}{T_{cr}}.\tag{3.6.3}$$

Now, for every type of gas, the factor Z only (approximately) depends on the reduced pressure and temperature. This principle is called the **principle of corresponding states**.

There are many (more complicated) equations of state. A few examples are the **Van der Waals Equations of State**, the **Beattie-Bridgeman Equation of State**, the **Benedict-Webb-Rubin Equation of State** and the **Virial Equation of State**. All the above equations of state have certain coefficients which need to be determined by experiments. Generally we can say that the more coefficients an equation has, the more accurate it is.

4. Closed Systems

4.1   Boundary Work

A **closed system** is, as was mentioned earlier, a system which can not exchange mass with its surroundings. The only way in which energy interaction with the surroundings is possible, is through heat transfer and by work. Therefore we can derive the **energy balance**, stating that

$$\Delta E = E_{in} - E_{out} = Q_{in} + W_{in} - Q_{out} - W_{out}. \tag{4.1.1}$$

Usually it is assumed that the heat Q flows inward and the work W is the work performed by the system (thus "flowing" outward). This reduces the energy balance to

$$\Delta E = Q - W, \qquad \Leftrightarrow \qquad \Delta e = q - w. \tag{4.1.2}$$

If the values of Q or W will turn out to be negative, then the wrong direction has been assumed.

4.2   Boundary Work

Let's take a closer look at the work. Work is force times distance. The force comes from the pressure inside the system. But to have a distance present, the boundary of the system must move. So there can only be work done if there is compression/expansion of the system. The corresponding type of work is called **moving boundary work**. The boundary work W_b can be found using

$$\partial W_b = F \, ds = PA \, ds = P \, dV \qquad \Rightarrow \qquad W_b = \int_1^2 P \, dV, \tag{4.2.1}$$

where V is the volume of the system. Note that the boundary work performed during a process per unit mass is simply the area under a $P - v$ diagram.

During processes, pressure and volume are often related by $PV^n = C$, with V still the volume and n and C constants. Any process of this kind is called a **polytropic process**. Using this relation (or, to be more precise, $P = CV^{-n}$) the boundary work can be found. Sometimes the coefficient n first has to be derived from the **polytropic efficiency** $\eta_{polytropic}$. This can be done using

$$\eta_{polytropic} = \frac{\gamma/(\gamma - 1)}{n/(n - 1)} \quad \text{if } p \text{ decreases, and} \quad \eta_{polytropic} = \frac{n/(n - 1)}{\gamma/(\gamma - 1)} \quad \text{if } p \text{ increases.} \tag{4.2.2}$$

The coefficient γ now does not denote the specific weight. It is the ratio of specific heats, which will be defined in the next paragraph.

4.3   Specific Heats

The **specific heat** is defined as the energy required to raise the temperature of a unit mass of a substance by one Kelvin. The amount of energy needed depends on the process. If the heating is done at constant volume, we find the **specific heat at constant volume** c_v. Identically, if the process is performed at constant pressure, we find the **specific heat at constant pressure** c_p. They can be found using

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \qquad \text{and} \qquad c_p = \left(\frac{\partial h}{\partial T} \right)_p. \tag{4.3.1}$$

For an ideal gas the internal energy u and the enthalpy h only depend on the temperature T. So the specific heats also depend on temperature only. Therefore we have

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T)\, dT \qquad \text{and} \qquad \Delta h = h_2 - h_1 = \int_1^2 c_P(T)\, dT. \qquad (4.3.2)$$

Usually the functions for c_v and c_p are unknown. However, there are tables with their values for given temperatures. So, what we then do, is take the value of (for example) c_v at T_1 and T_2, take their average, and use that value to calculate Δu. In an equation this becomes

$$\Delta u = \frac{c_v(T_2) - c_v(T_1)}{2}\,(T_2 - T_1) = c_{v,avg}\,(T_2 - T_1) \qquad \text{and identically} \qquad \Delta h = c_{p,avg}\,(T_2 - T_1)\,. \qquad (4.3.3)$$

There is an important relation between c_p and c_v. We know (from the definition of enthalpy and the perfect gas law) that $dh = du + R\, dT$. Differentiating with respect to temperature gives

$$c_p = c_v + R, \qquad (4.3.4)$$

where R is, as we already know, the gas constant for ideal gases. We can also define the **specific heat ratio** as

$$\gamma = \frac{c_p}{c_v}. \qquad (4.3.5)$$

Like the specific heats, also the specific heat ratio γ depends on the temperature T. The variation with temperature is very small though, so usually this ratio is assumed to be constant.

4.4 Incompressible Substances

An **incompressible substance** is a substance whose specific volume v is constant. Solids and liquids can be approximated as such substances. For such substances $R = 0$ and thus $c_p = c_v = c$. We now would like to know how these substances respond to changes. Or, to be more specifically, how does the enthalpy change during a process?

From the definition of enthalpy, we find that for incompressible substances

$$\Delta h = \Delta u + v\,\Delta P + P\,\Delta v = \Delta u + v\,\Delta P = c_{avg}\,\Delta T + v\,\Delta P. \qquad (4.4.1)$$

Note that the term $P\,\Delta v$ has disappeared, since v is assumed to be constant. For liquids, we can distinguish two special cases, being

- **Constant pressure processes** ($\Delta P = 0$) where $\Delta h = \Delta u = c_{avg}\,\Delta T$.
- **Constant temperature processes** ($\Delta T = 0$) where $\Delta h = v\,\Delta P$.

For solids the term $v\,\Delta P$ is insignificant, so all processes for solids can be approximated as constant pressure processes.

5. Control Volumes

5.1 Conservation of Mass

In the previous chapter we looked at closed systems. Now we look at control volumes. A **control volume** is a fixed volume in space, where mass can move through. Just like we have applied conservation of energy in closed systems, we can apply the **conservation of mass principle** in control volumes. So we have

$$\Delta m = m_{in} - m_{out}. \tag{5.1.1}$$

The **mass flow rate** $\dot{m}$ is the mass flowing through a cross-section per unit time. Suppose we have a pipe or duct. We can then determine the mass flow through this pipe using

$$\dot{m} = \int_{A_c} \rho \nu_n \, dA_c = \rho \nu_{n,avg} A_c, \tag{5.1.2}$$

where A_c is the cross-sectional area of the pipe and ν_n is the velocity of the flow normal to this area. Identically, we can define the **volume flow rate** $\dot{V}$ as

$$\dot{V} = \int_{A_c} \nu_n \, dA_c = \nu_{n,avg} A_c = \dot{m} v. \tag{5.1.3}$$

We can now rewrite the conservation of mass principle as

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}. \tag{5.1.4}$$

5.2 Energy of a Flowing Fluid

The interesting thing about a control volume, is that mass can enter it. What we want to know is how much energy is added to the system when a piece of mass enters a control volume. First of all, we know that the specific energy e consists of specific internal energy u, specific kinetic energy $V^2/2$ and specific potential energy gz. But there is more.

When a mass enters a control volume, something pushes it in. This pushing performs so-called **flow work** (also called **flow energy**), having magnitude

$$W_{flow} = PV, \qquad \text{or, expressed per unit mass,} \qquad w_{flow} = Pv. \tag{5.2.1}$$

So we find that the **total energy of a flowing fluid** per unit mass is

$$\theta = w_{flow} + e = Pv + u + \frac{1}{2}V^2 + gz = h + \frac{1}{2}V^2 + gz. \tag{5.2.2}$$

5.3 Steady Flow Processes

During a **steady flow process** the properties inside the control volume do not change with time. Since the total mass then is constant, we have $dm/dt = 0$ and thus

$$\dot{m}_{in} = \dot{m}_{out}. \tag{5.3.1}$$

If the flow is also incompressible, then also

$$\dot{V}_{in} = \dot{V}_{out}. \tag{5.3.2}$$

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For steady flow processes, also the energy stays constant. This implies that $\dot{E}_{in} = \dot{E}_{out}$, or equivalently,

$$\dot{Q}_{in} + \dot{W}_{in} + \sum_{in} \dot{m}\theta = \dot{Q}_{out} + \dot{W}_{out} + \sum_{out} \dot{m}\theta. \tag{5.3.3}$$

If we define $\dot{Q} = \dot{Q}_{in} - \dot{Q}_{out}$ as the heat that goes into the system and $\dot{W} = \dot{W}_{out} - \dot{W}_{in}$ as the work done by the system, we will get

$$\dot{Q} - \dot{W} = \dot{m}\left(h_{out} - h_{in} + \frac{V_{out}^2 - V_{in}^2}{2} + g\left(z_{out} - z_{in}\right)\right). \tag{5.3.4}$$

Dividing by $\dot{m}$ gives

$$q - w = h_{out} - h_{in} + \frac{V_{out}^2 - V_{in}^2}{2} + g\left(z_{out} - z_{in}\right), \tag{5.3.5}$$

where $q = q_{in} - q_{out}$ and $w = w_{out} - w_{in}$. There are many examples of steady flow devices in real life. For example, a **nozzle** is a device that increases velocity by decreasing the pressure. A **diffuser** does exactly the opposite. For both devices, the amount of heat transferred ΔQ, the amount of work performed ΔW and the change in potential energy Δpe can be neglected. This reduces the energy balance equation to

$$h_{in} + \frac{1}{2}V_{in}^2 = h_{out} + \frac{1}{2}V_{out}^2. \tag{5.3.6}$$

A similar thing can be done for other devices with a steady flow processes, such as **turbines** and **compressors**.

5.4   Unsteady Flow Processes

For many processes there are properties inside the control volume that change over time. Such processes are called **unsteady flow processes**. The relations of the previous paragraph are not applicable to those processes.

Dealing with unsteady flow processes is a lot more difficult. We therefore often assume that such processes are uniform flow processes. A **uniform flow process** is a process for which the properties at the inlets and outlets do not change with time or position.

Now let's look at two situations in this flow: One initial situation (1) and one situation a bit later (2). A heat Q has been added. The system has done an amount of work W. Also incoming mass has brought an energy $(m\theta)_{in}$, and mass leaving the system has taken energy $(m\theta)_{out}$ with it. Using these data, we can set up the energy balance for uniform flow processes. We get

$$Q - W + (m\theta)_{in} - (m\theta)_{out} = m_2 e_2 - m_1 e_1. \tag{5.4.1}$$

Once more this equation can be simplified, based on various assumptions.

6. Heat-Work Transformations

6.1   Reservoirs

In this chapter we'll take a look at how we can transform heat into work, and vice verse. But before we can go into details, we have to make some definitions.

We define a **thermal energy reservoir** (or just a **reservoir**) as a hypothetical body that can absorb/supply heat without any change in temperature. A reservoir that supplies energy in the form of heat is called a **source**. A reservoir that absorbs it is a **sink**.

6.2   Heat Engines

Work can be transformed entirely into heat. However, transforming heat to work is a bit troubling. So let's give that process a closer look. A device that converts heat to work is called a **heat engine**. A heat engine receives a heat Q_H from a high-temperature source. It converts part of the heat into work W_{out}. The remaining heat Q_L is dumped in a low-temperature sink. Using this data, we find that

$$W_{out} = Q_H - Q_L. \qquad (6.2.1)$$

The **thermal efficiency** η_{th} of a heat engine can now be found using

$$\eta_{th} = \frac{\text{Desired output}}{\text{Required input}} = \frac{W_{out}}{Q_H} = 1 - \frac{Q_L}{Q_H}. \qquad (6.2.2)$$

So what we need to do is make sure we need to dump as few heat as possible to the low-temperature sink. If possible, we would of course prefer to have $Q_L = 0$. But sadly this is not possible. This is because the **Kelvin-Plank statement** says that it is impossible for any device to receive heat from a single reservoir and produce work. Therefore the fraction Q_L/Q_H should simply be minimized. How this is done is something we will look at later.

6.3   Refrigerators and Heat Pumps

We saw that a heat engine uses temperature to create work. On the other hand, we can also use work to regulate temperature. A **refrigerator** is a device that transfers heat from a low-temperature region to a high-temperature region. The **Clausius statement** states that this transfer won't happen by itself. We therefore need to add work to get the desired effect.

We just saw that a heat engine produced work. A refrigerator, on the other hand, requires work W_{in}. Also, the direction of heat transfer is reversed. An amount of heat Q_L now comes from the low-temperature source, after which an amount Q_H goes to the high-temperature sink. So this time

$$W_{in} = Q_H - Q_L. \qquad (6.3.1)$$

To check how well a refrigerator functions, we now don't use an efficiency. Instead, the **coefficient of performance** of a refrigerator is defined as

$$COP_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}. \qquad (6.3.2)$$

The reason for using an other term than the efficiency, is because the coefficient of performance can be bigger than 1, while an efficiency can not.

A device very similar to a refrigerator is a **heat pump**. In fact, refrigerators and heat pumps are the same, except for their goal. While refrigerators want to keep the low-temperature source cold, heat pumps want to keep the high-temperature sink warm. The coefficient of performance of a heat pump thus becomes

$$COP_{HP} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_H}{W_{in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}} = COP_R + 1. \tag{6.3.3}$$

6.4 Reversible Processes

A **reversible process** is a process that can be reversed without leaving any trace on the surroundings. Processes that are not reversible are called **irreversible processes**. Reversible processes actually do not occur in nature. They are simply idealizations of actual processes. Reversible processes are always more efficient than irreversible processes.

Factors that cause a process to be irreversible are called **irreversibilities**. The most well-known irreversibility is **friction**. Also **heat transfer** over a finite temperature difference causes an irreversible process. A process is called **internally reversible** if no irreversibilities occur within the boundaries of the system during the process. Identically, a process is called **externally reversible** if no irreversibilities occur within the surroundings of the system. A process is **totally reversible** (or simply **reversible**) if it is both internally and externally irreversible.

6.5 The Carnot Cycle

We know that reversible processes are the most efficient processes. One example of a reversible process is the **Carnot cycle**, using a so-called **Carnot heat engine**. This cycle consists of four reversible steps.

First the heat engine is connected to an energy source at temperature T_H, causing **isothermal expansion**. The energy source is then replaced by an insulation, causing **adiabatic expansion**. After that, the insulation is removed, and an energy sink at temperature T_L is connected to the heat engine. This causes **isothermal compression**. Finally, the energy sink is once more replaced by insulation, causing **adiabatic compression**. This completes the cycle. In this cycle, heat has flowed from the energy source (at T_H) to the energy sink (at T_L), producing work W_{out}.

The funny thing about the Carnot cycle is that it can be reversed. Now work is added to the system, to transport heat from the (new) energy source (at T_L) to the (new) energy sink (at T_H). We then would have a **Carnot refrigerator**.

6.6 Quality of Energy

We could ask ourselves: How does the efficiency/coefficient of performance depend on the temperatures of the source and the sink? We know that the efficiency strongly depends on the factor Q_H/Q_L. For reversible processes, it can be shown that

$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}, \tag{6.6.1}$$

where $\phi(T)$ is a certain unknown function. Usually this function is assumed to be $\phi(T) = T$, resulting in

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}. \tag{6.6.2}$$

This makes the efficiency of a Carnot heat engine (the so-called **Carnot efficiency**)

$$\eta_{th} = 1 - \frac{T_L}{T_H}. \tag{6.6.3}$$

So if the source is much hotter than the sink, it's much easier to get work out of it. Identically, the coefficient of performance of the Carnot refrigerator now is

$$COP_R = \frac{1}{\frac{T_H}{T_L} - 1}. \tag{6.6.4}$$

So it gets increasingly hard to reduce the temperature of a sink, as it gets colder.

These conclusions give rise to an idea. It seems that very hot energy sources are much more valuable than less hot energy sources. Therefore, next to the quantity of energy, also the **quality** of energy matters. The higher the temperature, the higher its quality.