Cooling and Fermenting

9

9.1 Setting the Stage

At this point in the brewing process, the brewer has prepared a batch of *bitter wort* (wort that has been flavored with hops), boiled it, and added flavorings such as hops. The wort is hot and sterile and has just the right color, flavor, and amount of sugars. However, it is too hot to support the growth of yeast. The wort at this stage also has residue floating in it. The residue includes coagulated proteins, polyphenol-protein complexes, hop materials, and likely some grain materials that made it into the boil kettle from the mash tun. This material is known as *trub* (pronounced "troob"). The brewer does not want this in the beer; it simply does not taste good at all.

Getting rid of the un-dissolved material is essential to ensuring that the fermentation in the next step proceeds smoothly. The yeast during fermentation will flocculate (clump and precipitate from the solution) as the process proceeds. The presence of "floaties" in the wort will interfere with this process. In addition, the un-dissolved material that remains in contact with the wort can continue to impart flavors into the wort. This means that the wort could continue to extract tannins and other flavored compounds from the hops. In fact, this could severely damage the finished beer.

So, the brewer works to remove these solids from the wort. The easiest way to do this is to swirl the wort while it is still in the boil kettle. In the smallest vessels, the brewer could simply stir the wort with a large paddle. In vessels of any size over about 1 bbl, pumping the wort from the bottom edge of the kettle and returning it back into the vessel at an angle help to clarify the wort. Continuous pumping in a tangential manner causes the entire vessel to swirl.

After 10–20 min of whirlpooling the wort while it is still hot, the pumping stops. But the brewer does not do anything yet. They tend to wait another 10–20 min to allow the whirlpooling to slow down to the point where the liquid is barely moving. While the wort swirls, the solids move inward to the center of the liquid and then form a pile right in the center. So, how does this work?

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As the wort swirls, the water molecules move very quickly at the outside of the vessel and very slowly at the center. In order to maintain movement in a circle, there must be a force that pushes against the fluid to keep it moving in a circle. In a swirling pool of liquid, that force is provided by the walls of the container—a centripetal force (and not centrifugal). Centripetal means "pointing inward," and an inward force is required to direct the fluid in a circle. These concepts are often confused because it depends on the frame of reference for the observer. If one is moving with the water, one feels a "centrifugal" force. The basic result is that the water becomes deeper on the outside edge than in the center. Try it and see; when you quickly stir a cup of water, the water gets deeper at the edges. This concept is use in centrifuges—a *device* to separate fluid components of different densities. The heavier material tends to settle out at the outside of the spinning circle.

At this point, the suspended solids in the hot wort move slowly toward the center of the whirlpool. If this movement was based only on the "centrifuge effect," we would expect the heavier suspended solids to collect on the outside of the vessel. What's the difference between a centrifuge and the boil kettle? The fluids in the centrifuge cannot mix and those fluids closer to the center of the circle are forced to rotate at the same angular speed as the fluids at the outside. In the boil kettle, due to liquid sheer forces, the fluids at the center of the circle rotate at a different angular speed. This, in combination with Coriolis forces, will tend to move solid particulates inward. In the end, the particles arrive near the center of the whirlpool and settle to the bottom of the vessel. For the brewer, the whirlpool results in a cone-shaped pile in the center of the vessel that contains all of the sediment. The liquid can then be removed from the outer edge of the vessel and pumped to the next step in the brewing process. The sediment remains behind and can be separated by withdrawing it from the valve located at the center of the vessel. Whirlpooling is a very necessary step that does not require any additional equipment.

9.2 Wort Chilling

After the trub has been removed from the wort, the next step in the process is to ferment the sugars. However, this occurs at a much lower temperature than the boil. Often the temperatures needed for the start of fermentation are in the range of 18–22 °C (65–72 °F), very much dependent upon the style of beer and yeast used in fermentation. The cooldown from boiling (100 °C, 212 °F) must occur aseptically and rapidly.

As the bitter wort cools, it is vulnerable to infection from microbes that would ruin the finished product. In fact, the bitter wort is the ideal growth medium for wild yeasts, bacteria, and other microorganisms. We do not want these microbes anywhere near the wort, because they can begin growing in the nutritious liquid. At the very best, any of these microbes would change the flavor of the beer. At the worst, the microbes could be harmful pathogens (very rare). The exception to the rule to keep everything out of the wort resides in the style of beer we want to make.

Farmhouse ales were and continue to be traditionally made by spontaneous fermentation with airborne yeast. In such a case, we would cool the hot wort in open tanks, invite whatever microbe that happens to be in the area, and hope for the best in the final taste. This style aside, brewers typically like to have full control over the final taste profile.

So, the bitter wort should be cooled as rapidly as possible, to avoid inoculation with some unwanted microbe. This process is achieved through the use of heat exchangers.

9.2.1 Heat Exchangers

A heat exchanger, quite simply, is a device that transfers heat from a hotter fluid to a cooler fluid by heat conduction. If we wanted to cool down a tepid glass of water, we could just drop ice into it. But we do not want to water down our beer with ice! So, the heat exchanger was designed to keep the two fluids separate. For example, the two liquids could be hot wort and cold water as in the case of wort cooling, cold glycol and fermenting beer, or it could be our final beer and steam in the pasteurization process. In all of these cases, we are transferring heat energy from one fluid to another *by conduction* through a material that separates them. So, we will start by reviewing the physical process of heat conduction. We initially discussed this in Chap. 8, but here we will delve into the subject in event greater detail.

Thermal heat conduction between two materials, that is to say energy transfer, occurs when the materials are in physical contact. The second law of thermodynamics requires this energy to flow from the object with the greater temperature to the object with the lower temperature. It stands to reason that there will be zero heat transferred if the two objects are at the same temperature.

Let us consider a simple system in which we have a rectangular bar of material in contact with a hot object on one side and a cold object on the other side as illustrated in Fig. 9.1. These hot and cold "objects" will later be our hot wort and cold water, for example. The rate of heat transfer, defined as the heat energy Q moved in time t and measured in watts, is given by *Fourier heat equation*:

$$Q/t = -\kappa A \frac{\Delta T}{\Delta x} \tag{9.1}$$

where

Q/t is the heat energy (Q) moved in time (t) with units of watts (W),
ΔT is the temperature difference across some slice of the bar, and
Δx is the thickness of the material.

If the material is a simple rectangular bar, these become the hot and cold temperature differences and the length of the material (d in Fig. 9.1), respectively. The cross-sectional area of the bar is given by A. The final term, κ, will be explained

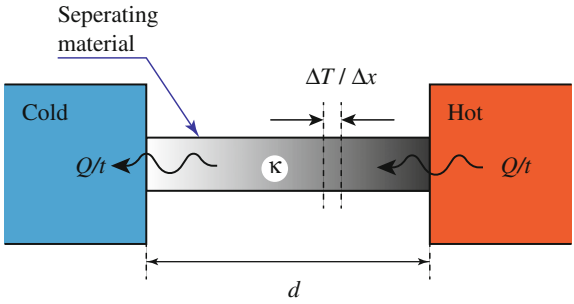

Fig. 9.1 Simple system viewed from the side to illustrate heat conduction physics in a *rectangular bar* of material separating a hot object and a cold object

later. The minus sign is in the equation to ensure that a positive heat flow goes into the cold object for a temperature difference (ΔT) defined as the hotter temperature minus the colder temperature.

There are a few things we can learn immediately from Fourier heat equation. If we make the material separating the two objects very thin, i.e., make d very small, then we make the heat transfer process faster and therefore more efficient. Alternatively, we could make the cross-sectional area of the connecting bar very large. A very basic heat exchanger system might have the hot fluid moving through the inside of a tube and the cold fluid on the outside of the tube. So, we can make the heat exchange faster and more efficient if we used a very long (large area), thin-wall (small d) tube.

Finally, the symbol κ is the thermal conductivity of a given material. This was first introduced in Chap. 8. This is a material-specific value which must be determined empirically. A list of thermal conductivities for some common materials is shown in Table 9.1. The thermal conductivity value tells us how well a certain material will conduct heat, and generally, the larger the number is, the better the material acts as a heat conductor. Looking at Table 9.1, silver is one of the better heat conductors. It is also a noble metal, meaning that it is not very reactive. So why

Table 9.1 Thermal conductivities of common materials at 20 °C

Material	κ (W/m K)
Water	0.6
Stainless steel	14
Tin	67
Brass	122
Aluminum	205
Copper	380
Silver	429

not make our heat exchangers from silver? In addition to its expense, silver is not very strong. So, the material would need to be thicker to improve its strength. This definitely underscores the impracticality of a silver heat exchanger.

Stainless steel, a common material that you would find in the brewery, has the poorest thermal conductivity. So why make a heat exchanger from stainless steel instead of copper, which is the next best thermal conductor? The reasons mimic those that we explored in the hunt for the perfect metal from which to make our boil kettle. Stainless steel is relatively easy to clean and is not reactive with the somewhat acidic wort and beer that we pump through the system. Moreover, since stainless steel is stronger than copper, we can make the separating material much thinner than if we use copper. So, we can make the net thermal conduction approximately equivalent.

As an example to highlight an important concept later, let us consider a special container in which we can place a thin rectangular plate of dividing material. On either side of the dividing material, we have identical isolated voids to hold water. On one side of the divider, we hold 1 kg of water at 100 °C, and on the other side, we hold 1 kg of water at 20 °C. The question is, due to heat conduction through the dividing material what is the final temperature of both sides and how long does it take for this to happen? We are going to make some assumptions, which will not take away from the final message. First, we will assume that the water on either side is well mixed, so we do not worry about heat conduction through the water. We also assume that there is no heat conduction to the rest of the world. Finally, to answer this question, we will need to make some assumptions about the divider. Let us assume it is a piece of thin (0.1 mm) copper with a surface area of 10 cm^2. Equation 9.1 tells us the *initial* energy transfer rate since the temperature difference is 80 K (determined by converting each temperature to kelvin and then taking the difference):

$$\begin{aligned}\frac{Q}{t} &= \frac{-401\ \mathrm{W}}{\mathrm{m\ K}} \times 0.001\ \mathrm{m}^2 \times \frac{80\ \mathrm{K}}{0.0001\ \mathrm{m}} \\ &= -4010 \times 80\ \mathrm{K} \\ &= 320{,}800\ \mathrm{J/s}\end{aligned} \tag{9.2}$$

So, in 0.05 s, 16,040 J of energy is transferred from the hot side to the cold side (i.e., 320,800 J/s × 0.05 s = 16,040 J). What does that do to the temperature of each side? It will raise the temperature of the cold side and lower the temperature of the hot side. We can find by how much. Recall that the specific heat of water c = 4181 J/kg K, and the temperature change is related to the quantity of heat energy removed or added:

$$Q = mc\Delta T. \tag{9.3}$$

CHECKPOINT 9.1
If 16,040 J of energy is added to the cold side at 20 °C, what is the new temperature? If 16,040 J of energy is removed from the hot side at 100 °C, what is the new temperature?

So, now what is the heat transfer rate with the new temperatures? Will we still transfer 320,800 J/s? Because the temperature difference is smaller, the heat transfer rate will be smaller. This further means that the change in temperature will be smaller. If we continue this analysis using 0.05s time steps, it is easy to develop a spreadsheet to calculate the temperatures after every time step. Table 9.2 shows a partial listing of such a calculation, and Fig. 9.2 illustrates this table graphically. *Note that we will need to wait a relatively long time to reach thermal equilibrium.* The main point of this exercise is to underscore that the heat transfer rate is greatest when the temperatures of the two different fluids are greatest. But, as we exchange heat, as in a heat exchanger, the temperature difference becomes smaller and smaller which then means that the transfer rate also becomes smaller.

Table 9.2 Estimated temperature as a function of time for two 1 kg portions of water in thermal contact with a thin copper sheet

Time (s)	T_{hot} °C	T_{cold} °C	Time (s)	T_{hot} °C	T_{cold} °C
0	100.000	20.000	3.55	60.031	59.969
0.05	96.164	23.836	3.6	60.028	59.972
0.1	92.695	27.305	3.65	60.025	59.975
0.15	89.559	30.441	3.7	60.023	59.977
…	…	…	…	…	…

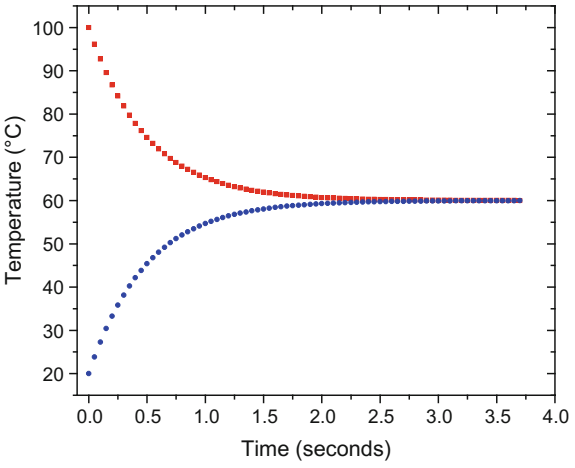

Fig. 9.2 Estimated temperature as a function of time for two 1 kg portions of water in thermal contact with a thin copper sheet. Based on the data from Table 9.2

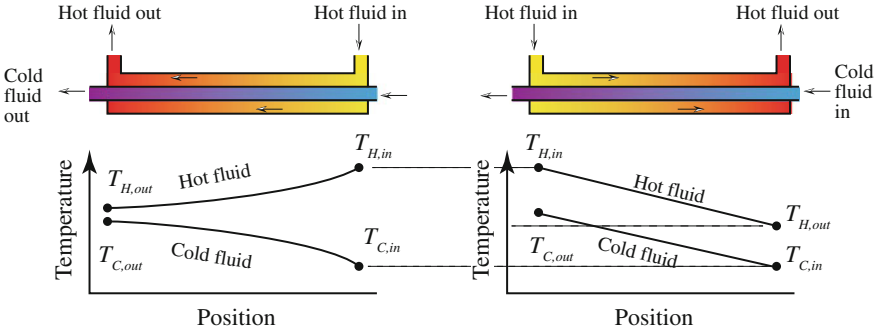

Fig. 9.3 Countercurrent flow (*left*) and concurrent flow (*right*) heat exchangers. Note that the inlet temperatures are the same for both configurations

There are a variety of heat exchanger configurations. Again, recall that the idea is to exchange heat energy between two fluids without mixing the two. Let us start with the simplest heat exchanger construction in which the cold fluid flows through the inside of a tube and the hot fluid is constrained to flow along the outside of this tube. This basically means we have a double-wall tube arrangement. We now encounter our first design consideration. We could have the two fluids run parallel to each other, or in opposite directions. These two different types of heat exchangers are classified as either concurrent flow or countercurrent flow (respectively), as illustrated in Fig. 9.3.

In the concurrent flow heat exchanger, the rate of energy transfer is greatest at the point where both the hot fluid and cold fluid enter the tubes because the temperature difference is greatest. However, as the temperatures become closer together, the rate of heat transfer is reduced. The rate of heat transfer keeps getting smaller as the temperatures get closer and closer. This means that the exit temperature of the hot fluid $T_{\mathrm{H,out}}$ can never be lower than the exit temperature of the cold fluid $T_{\mathrm{C,out}}$. Therefore, the heat transfer is restricted by the cold fluid's outlet temperature.

In the countercurrent flow heat exchanger, there is always a temperature difference along the length of the exchanger. One benefit of this arrangement arises because the temperature difference is more or less the same along the length of the system. Therefore, the thermal (mechanical) stresses in the device are reduced. This net temperature difference also means that it is possible for the exit temperature of the hot fluid to be *less than* the exit temperature of the cold fluid. And this must be considered, because if the temperature of the hot fluid gets too cold, it may freeze into a solid. This would be possible if the cooling fluid's inlet temperature is lower than the freezing point of the hot liquid. It does not seem like this would be an issue, but often cold beer needs to be cooled to just below 0 °C (32 °F). It should not freeze at this temperature because it is a mixture of alcohol and water, but if the temperature gets much lower than this, it could.

Generally speaking, a countercurrent flow heat exchanger will be more efficient at heat transfer for a given flow rate through the tubes. This does not mean that we would never use a concurrent flow exchanger. The large temperature difference at the inlet means that we can achieve a very rapid change in temperature. If either of the fluids is changing phase, such as steam condensing into water, then the heat exchange occurs isothermally (at the same temperature) and it does not matter which exchanger we use.

There are a variety of mechanical implementations of heat exchangers and they are classified by their construction. The two basic types are the tube and shell heat exchanger and the plate heat exchanger. An example of tube and shell heat exchanger is shown in Fig. 9.4. It is constructed of a bundle of small tubes that carry one of the fluids. This assembly is contained within a shell, and the second fluid flows around the outside of the tubes. Sometimes, these heat exchangers will have extra baffles to direct the second fluid around the tubes. The path of the fluids shown in Fig. 9.4 does not quite fall into either a countercurrent flow or a concurrent flow arrangement. While the second fluid generally flows counter to the first fluid, its path is classified more as a *cross-flow* as it flows around the baffles.

Among the tube and shell heat exchangers, we can have variety. By adding baffles and changing where the fluids enter and exit, we can create, for example, the two-pass tube-side heat exchanger in Fig. 9.5.

A plate heat exchanger is constructed from many thin plates, stacked together with a small space between each plate. Gaskets placed around the edges of the plates, as shown in Fig. 9.6, maintain the spacing between each plate. The plates have four openings at each corner, and the gaskets are placed such that the flow of hot and cold fluids alternates between plates. Because the surface area of the plates is quite large, and because the plates can be made from a very thin material, plate heat exchangers can be incredibly efficient at transferring energy. Plate-type heat exchangers are easier to disassemble and clean compared to a shell and tube heat exchanger. This can be a benefit to a brewery.

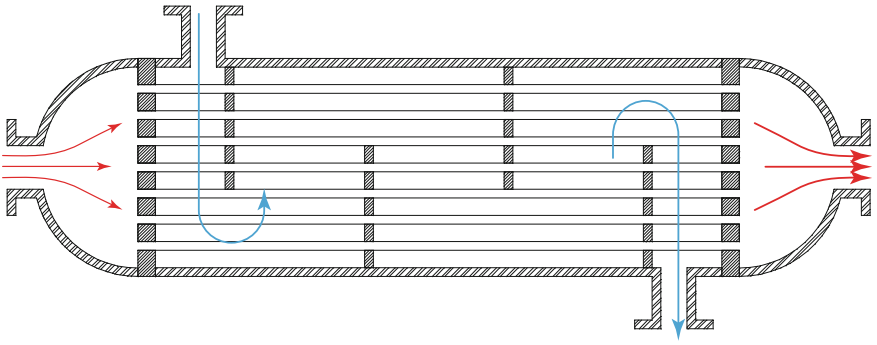

Fig. 9.4 Shell and tube heat exchanger

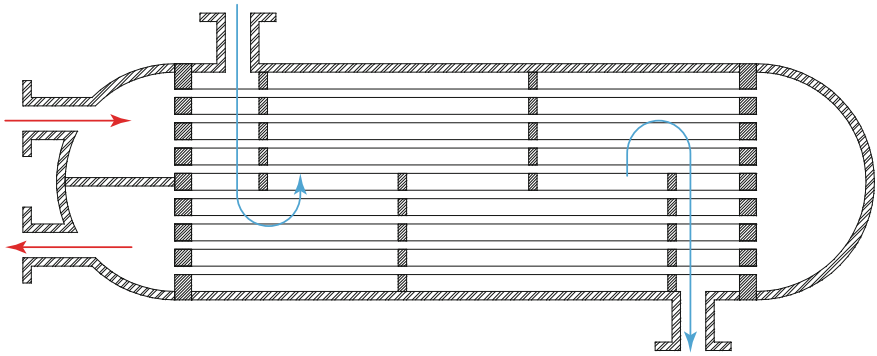

Fig. 9.5 A two-pass shell and tube heat exchanger

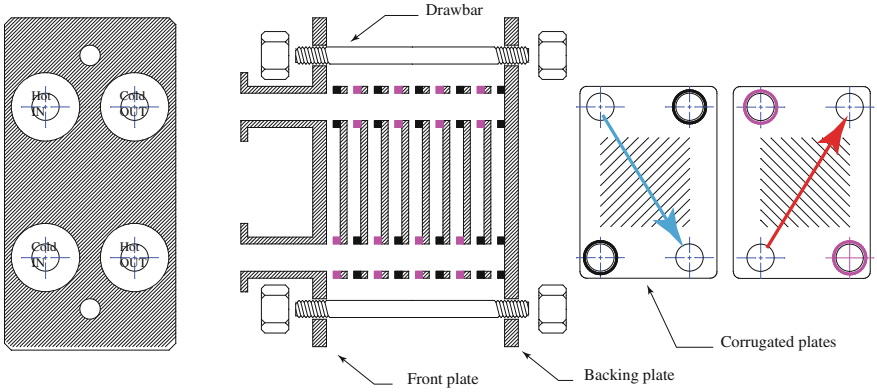

Fig. 9.6 Plate-type heat exchanger. The *red* and *blue arrows* show the flow of the cold and hot fluids (respectively) in alternating plates

Fluid flow inside a plate heat exchanger appears to be complex. It is not. Figure 9.7 illustrates the flow in a plate heat exchanger. We can think of how the liquid flows through the system as if we had a double-decker sandwich. The hot liquid flows in one part—i.e., one half of the sandwich, and the cold liquid flows in the other part—i.e., the other half of the sandwich. Gaskets keep the flow of the two liquids separate so that they never physically touch each other, but because the two liquids are in contact with the same plate (the middle piece of bread in our double-decker sandwich), heat transfer can occur. The plate heat exchanger can be set up to allow a countercurrent flow or a concurrent flow pattern.

Typical plate heat exchangers are arranged so that the hot wort (still above 190 °F after the whirlpool) flows into the exchanger and are cooled to 70 °F without much reduction in the flow rate. Because of the small openings and winding path of the wort as it goes through the plate heat exchanger, a large backpressure develops when the liquid flows (i.e., the pump must develop a large positive delivery head). Care

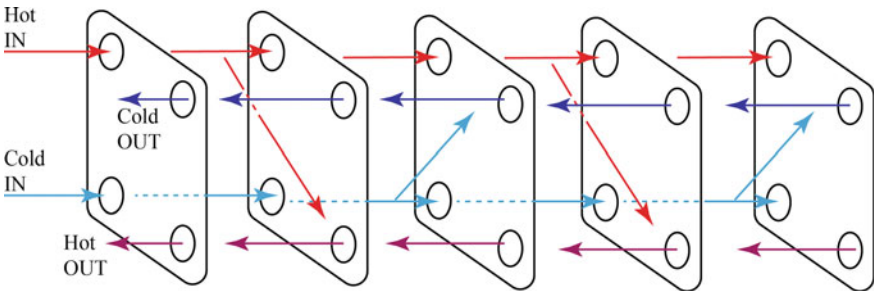

Fig. 9.7 Flow patterns in a plate-type heat exchanger. The *red* and *blue arrows* show the flow of the cold and hot fluids (respectively) in alternating plates. Is the overall system shown here representative of a countercurrent flow or a concurrent flow?

must be taken to ensure that the pumps used are capable of supplying this head without causing cavitation.

9.3 Equipment Used in Fermentation

Once the wort has been cooled to an appropriate temperature to support yeast growth, oxygen gas is added to the liquid. Because gases are much less soluble in hot liquids than cold liquids, the boiling process has removed all of the oxygen from the wort. The addition of oxygen is necessary to support the growth stage of the yeast that will be added in the fermenter. There are many different ways to add oxygen to the wort. These methods include (a) pumping the cool wort into an open vessel and allowing air to dissolve into the wort, (b) splashing or spraying the wort into a vessel that is full of air, (c) bubbling oxygen gas into the fermenter, and

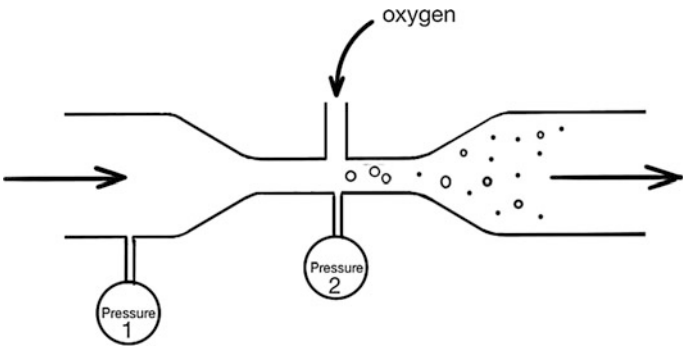

Fig. 9.8 Venturi aerator. The pressure at point 1 is greater than the pressure at point 2 because the liquid flowing in the pipe must increase its velocity in the restriction. This makes the perfect location in which to add oxygen

(d) passing the wort through a *Venturi aerator* (Fig. 9.8). Each of these methods attempts to bring the oxygen level in the wort up to about 8–10 ppm.

Some brewers prefer using a Venturi aerator to oxygenate their worts. This device is basically a tube that has a restriction in the flow of the wort by changing the pipe diameter. As the liquid enters the smaller pipe diameter, the velocity of the liquid increases. Because the velocity of the liquid increases, the pressure of the liquid decreases. A small hole in the center of the small pipe is used to inject oxygen into the flowing wort. The low pressure where the oxygen is injected means that bubbles of air (or oxygen) enter the wort at this stage. Immediately after the small diameter pipe, the pipe returns to its normal size. The velocity of the wort slows down and the pressure increases. Because the pressure increases, the tiny air or oxygen bubbles that are dispersed in the wort quickly dissolve.

The best way to inject oxygen into the wort, however, is by bubbling it directly into the fermenter using an "oxygenation stone." The stone is basically a porous tube that forces the oxygen to bubble as very tiny bubbles. These bubbles have a much better chance of being dissolved in the wort.

If air is used to deliver oxygen to the wort, the maximum amount that can be physically dissolved is only 8–10 ppm. But, other issues with the use of air exist. For example, if air from the room is used, a sterilization process must be put into place so that no bacteria or other flavor-harmful microbes get added into the wort. If pure oxygen is used, the amount of gas that is soluble in the wort rises to about 9–10 ppm. Keep in mind that oxygen is not terribly soluble in wort, so it is very difficult to get above this concentration of oxygen at the temperatures we are using. And if a brewer tries to do so, the oxygen will simply bubble out of solution in the fermenter. This is likely not a great thing, because a lot of oxygen trapped in the headspace above the fermenting wort may result in the oxidation of the wort.

Once oxygenated, the wort is pumped into the fermenter and yeast is added. The style of fermenter plays a very large role in the flavors of the finished product and in how yeasts are collected for use in other batches. In the remaining parts of this section, we will uncover the different types of fermenters.

9.3.1 Refrigeration

Many times in the brewing process, we need temperatures cooler than the ambient surroundings or we need to cool a process, such as fermentation, that generates heat. When cooling our hot, bitter wort from the boil kettle, it is a straightforward process to use a heat exchanger and use available room temperature water to cool it. Speaking from a thermodynamics perspective, we are transferring thermal energy (heat) from the hot, bitter wort to the much cooler water. The second law of thermodynamics allows this process, transferring energy from the hotter object to the cooler object. But, what if we wanted to cool something, like a fermenter or a storage room, to a temperature *less than* the ambient surroundings? The second law of thermodynamics does not permit heat energy to spontaneously and freely move from a cooler area (e.g., the storage room) to a warmer area. As we will see in a

moment, moving heat energy from a colder environment to a warmer environment requires effort (work).

Let us consider an analogy of this process. Assume that a small tube and a valve connect two identical containers of water. One container has much more water in it, and thus, the water level is much higher in the container. When we open the valve, the water in the container with the highest level begins to flow until the levels are equal. We would never expect water to flow "uphill" in the other direction. This idea is the same as heat transfer. In fact, the equations describing this transfer of water are identical to the example we discussed surrounding (Fig. 9.2). If we wanted water to flow from the lower level to the higher level, we need to install a pump to do this work. The same idea is true in *thermodynamics*. We will use a "heat pump" to move heat energy from a region of lower temperature to that of higher temperature against the natural tendency of heat to flow from the higher temperature object to the lower temperature object.

A "heat pump" that removes heat energy from an object (thus cooling it) and moves it to somewhere else is commonly called a *refrigerator*. To understand how these devices work, let us explore some general thermodynamic processes first. A useful place to start is on the subject of thermodynamic engines, which convert heat energy into useful work. Further, we will simplify our discussion for the moment by assuming that we are working with an ideal, mono-atomic gas.

9.3.1.1 Introductory Thermodynamics: State Variables and Processes

Consider a cylindrical chamber that has a movable piston, which can change the internal volume V as in Fig. 9.9. We will assume that the chamber does not leak and contains a given number of moles of gas atoms, n. Further, we will assume that the gas is at some temperature T and exerts a net pressure P on the walls of the chamber. Assuming that the gas is ideal, these parameters are related through the ideal gas law

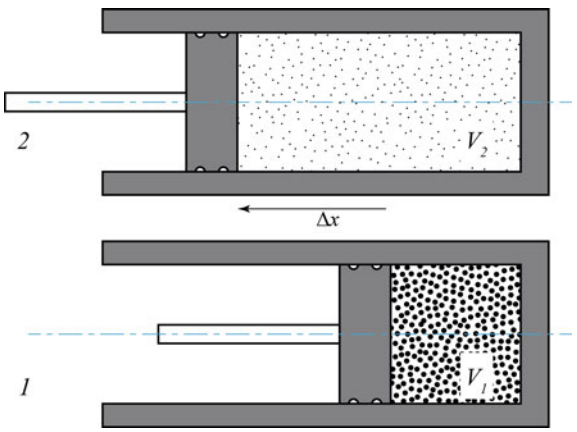

Fig. 9.9 An ideal gas in a cylindrical piston

$$PV = nRT. \tag{9.2}$$

where R is the ideal gas law constant, $R = 8.314\ \text{m}^3$ Pa/mol K. V is in cubic meters, P is in pascals, n is in moles, and T is in kelvins.

In thermodynamics, the variables (T, P, V, and n) in the ideal gas law equation (Eq. 9.2) are called *state variables* and the equation itself is an *equation of state*. As the term implies, these variables describe the state of the gas as it is and do not depend on the process that was taken to arrive at that particular set of conditions for the gas. We will introduce more state variables later, but a complete set of state variables completely describes the gas independent of its past history.

9.3.1.2 Internal Energy and the First Law of Thermodynamics

As long as the gas in Fig. 9.9 is not at absolute zero (0 K), the molecules of gas in the piston will exhibit random motion. The distribution of the "random" speeds of the gas molecules will depend on the temperature and mass of the molecules. This is the origin of thermal energy—the internal motion of the molecules. The gas can also have other avenues of storing and exchanging energy, such as rotational motion for the case of diatomic and larger molecules, or vibrational motion; it is as if the molecules were connected by springs. All of these various internal forms of energy are symbolized by a state function that has the symbol U, *internal energy*. When we *heat* (Q, thermal energy) the gas, we expect the internal energy to change. But we might also use this internal energy to do useful *work* (W). The *first law of thermodynamics* is basically a rule about the conservation of energy:

$$\Delta U = \delta Q - \delta W. \tag{9.3}$$

This equation says, in words, that the *change* in the internal energy of a system is equal to the incremental amount of heat put into the system, minus the incremental work done by the system on the environment (and not the other way around). Since the laws of thermodynamics were developed in connection with developing efficient steam engines, it would make sense to think about the work ***output*** of a system. Note as well that we can only address changes in the internal energy. We usually do not care about the total stored energy in a system, because the changes in energy are what we can observe. Finally, the quantities δQ and δW are not state variables.

9.3.1.3 Thermodynamic Processes

In engines and refrigerators, the working material (a gas in the present discussion) will undergo cycles, following specific processes. Let us consider a variety of process and then see how putting these together will give us an engine or refrigerator. This can be done by applying different processes to a gas in a piston and seeing what comes out of the process. Our selection of processes will be cyclical in nature so that the gas ends up in the same state as we started.

To start, let us first reconsider our piston in Fig. 9.9. Let us assume that the chamber holds 0.1 mol of gas atoms (i.e., $n = 0.1$ mol). The piston starts in position

1 with a volume of 0.01 m^3 (i.e., $V_1 = 0.01\ m^3$), and we want the gas to expand, moving the piston to position 2 where $V_2 = 0.1\ m^3$. If we do this in a way such that the pressure remains constant, the process is called *isobaric*. Note that as the piston moves from position 1 to position 2, the volume increases.

CHECKPOINT 9.2
In the isobaric process discussed above, what must happen to the temperature of the ideal gas as the volume increases while the pressure stays the same? If we assume that the pressure $P_1 = 20{,}000$ Pa, what are the two temperatures (beginning of the process and end of the process)? (Use the ideal gas law.)

Since the gas exerts a constant pressure as it moves, we can find the work done on the external environment. From the definition of work (see Chap. 7),

$$\begin{aligned} W &= F \cdot \Delta x = P \cdot A \cdot \Delta x \\ W &= P \cdot \Delta V \end{aligned} \tag{9.4}$$

In this equation, A is the cross-sectional area of the piston. The important point is that the gas has done useful work on the piston, which could be connected to something else and do work on the outside environment. As we discovered in the checkpoint, there must be an increase in temperature for this to happen, which will require the addition of some thermal energy to the gas. This change in *state* of the system is commonly shown graphically on a pressure–volume (PV) diagram, such as the isobaric process in Fig. 9.10. Note that, considering Eq. 9.4, the area under the curve from state X to state Y (or position 1 to position 2) is equal to the work done. Also, this is ***positive*** work (on the environment) since the force exerted on the environment (the piston) is in the same direction as the displacement.

The amount of heat energy required for this process can be calculated based on the heat capacity ideas presented in Chap. 8. For an ideal, mono-atomic gas, the

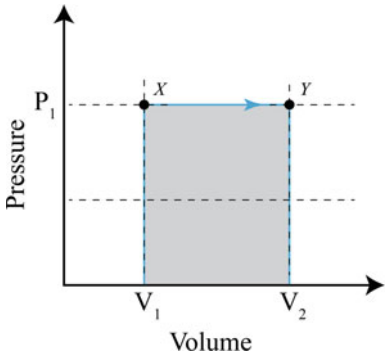

Fig. 9.10 State variables as an ideal gas undergoes an isobaric process from volume V_1 to V_2. The *states* are labeled X and Y, respectively

constant pressure specific heat capacity $c_P = \frac{5}{2}R$, so the amount of heat energy which must be added to the system for isobaric processes is given by inserting this equation into a version of the heat capacity equation (Q = m c ΔT):

$$\delta Q_P = n\left(\frac{5}{2}R\right)\Delta T. \tag{9.5}$$

where δQ_P is the change in the heat energy when the pressure is constant.

CHECKPOINT 9.3
Calculate the work done and the heat energy put into the system for the above isobaric process. Using the first law of thermodynamics, what is the change in the internal energy of the gas?

An *isochoric* process is one in which the *volume* is held constant. Imagine now that we lower the pressure in the piston chamber, but manage to hold the volume constant. Reviewing the ideal gas law, this means that we will need to lower the temperature of the gas in order to change the pressure of the system. The result would be that we would have to remove the thermal energy. We will address that in a moment, but for now consider the work done on the external environment. Since the change in volume ΔV is zero, the work done is zero. The change in state variables P and V for the gas is shown in Fig. 9.11. It is important to note that the gas is not physically moving around on the PV diagram; the only thing changing is the pressure and temperature of the gas.

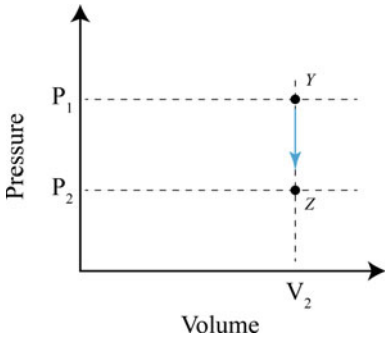

Fig. 9.11 State variables as an ideal gas undergoes an isochoric process from pressure P_1 to P_2. The *states* are labeled Y and Z, respectively. Zero work is done on the environment

For an ideal, mono-atomic gas, the constant volume specific heat capacity $c_V = \frac{3}{2}R$, so the amount of heat energy that must be added in order to get an isochoric process to occur is given by:

$$\delta Q_V = n\left(\frac{3}{2}\mathrm{R}\right)\Delta T. \tag{9.6}$$

CHECKPOINT 9.4
Assume that the final pressure at state *Z* is 2000 Pa. What is the temperature of the gas at this pressure? What is the change in the heat energy of the gas? Using the first law of thermodynamics, what is the change in the internal energy of the gas?

Finally, let us consider a process in which both the pressure and the volume change, but do it in such a way that the temperature remains constant. Processes that keep the temperature constant are called *isothermal* processes. Rearranging the ideal gas law,

$$P = nRT\left(\frac{1}{V}\right), \tag{9.7}$$

we see that the pressure is proportional to *1/V*. A representative isothermal curve is shown in Fig. 9.12. Actually, we can generate different families of curves that have different temperatures. Just keep in mind that any point on a given curve on the *PV* diagram has the same temperature. Each of these curves is known as an *isotherm*, where the temperature remains constant.

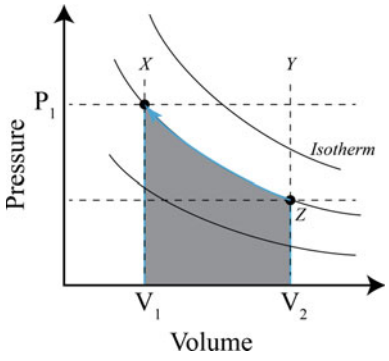

Fig. 9.12 State variables as an ideal gas undergoes an isothermal process from state *Z* to state *X*

CHECKPOINT 9.5
Of the three isotherms (lines of constant temperature) shown in Fig. 9.12, which one has the greatest temperature? …the smallest temperature? What is the temperature for the path indicated from state *Z* to state *X*?

The work done in an isothermal process is a bit more difficult to calculate, as it requires integral calculus. The steps are shown here for those that are interested, but the final result is the most important thing to remember. Starting from the definition of work and considering very small changes in volume dV, a small amount of work done is given by:

$$\delta W = P \cdot \mathrm{d}V. \tag{9.8}$$

Next, we insert the ideal gas law relationship for pressure. So, the total work done is:

$$W = \int_{Vi}^{Vf} nRT\left(\frac{\mathrm{d}V}{V}\right), \tag{9.9}$$

Carrying out the integration from the initial volume (V_i) to the final volume (V_f), we get the important result:

$$W = nRT \cdot \ln\left(\frac{V_f}{V_i}\right). \tag{9.10}$$

This is the area under the isotherm in Fig. 9.12. In this particular process from state *Z* to state *X*, note that the initial volume is larger than the final volume.

CHECKPOINT 9.6
Since the initial volume in state *Z* is 0.1 m^3 and the final volume in our isothermal process, state *X*, is 0.01 m^3, is the work done positive or negative? What is the work done? Since the internal energy depends only on the temperature, what is the change in the internal energy (ΔU) for an isothermal process? Given the first law of thermodynamics, what is the change in the heat energy for the gas?

If you have been keeping track with the processes to the example gas in our piston, we have returned the gas to the exact same state. At the end of this one cycle, we have absorbed 4500 J of heat energy from a heat source, rejected a total

Table 9.3 Summary of changes made to the example gas

State	State variable				
	P (Pa)	V (m^3)	T (K)	Work (J)	Heat (J)
X	20,000	0.01	241		
Isobaric process to				1800	4500
Y	20,000	0.1	2406		
Isochoric process to				0	−2700
Z	2000	0.1	241		
Isothermal process to				−461	−461
X	20,000	0.01	241		

of 3161 J to a cooler object (recall we must have a temperature difference for heat to flow) and did 1339 J of work in the process. This is summarized in Table 9.3 and graphically in Fig. 9.13. We have just described what is known as a *heat engine*; a system that takes heat energy from a hot object or environment does useful work and then outputs heat to a colder environment. The heat engine described in the example is a thought experiment. No mention was made on how to actually implement this.

The efficiency of most processes can be defined as the ratio of "what you got out" to "what you put in (or paid for)." In the heat engine, the work is what we got out of the device and we had to put in a certain amount of heat energy. So, we can define efficiency (η) as:

$$\eta = \frac{W}{Q_{\text{in}}}, \tag{9.11}$$

and in the present example, the efficiency is $\eta = 0.42$ or as a percent; 42 %. All heat engines must reject heat to a cooler environment; this is unavoidable.

Table 9.4 summarizes each of the equations that we have discovered during our exploration of a heat engine. Two additional processes, adiabatic and isentropic, are also listed in the table for reference.

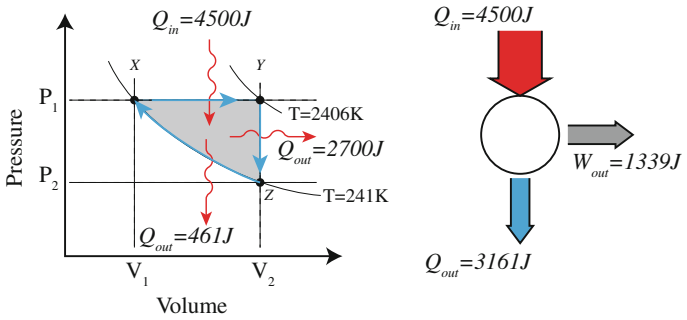

Fig. 9.13 Summary of isobaric, isochoric, and isothermal processes applied to the example mono-atomic gas

Table 9.4 Summary of thermodynamic processes

Process		Work done	Internal energy ΔU	Heat δQ
Isobaric	$\Delta P = 0$	$W = P(V_f - V_i)$	$\Delta U = \delta Q - \delta W$	$\delta Q* = nR\frac{5}{2}\Delta T$
Isochoric	$\Delta V = 0$	$W = 0$	$\Delta U = \delta Q$	$\delta Q* = nR\frac{3}{2}\Delta T$
Isothermal	$\Delta T = 0$	$W = Nk_B T \cdot \ln\left(\frac{V_f}{V_i}\right)$	$\Delta U = 0$	$\delta Q = \delta W$
Adiabatic	$\delta Q = 0$	$W = \frac{K\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right)}{1-\gamma}$	$\Delta U = -\delta W$	$\delta Q = 0$
Isentropic	$\Delta S = 0$	Reversible adiabatic		$\delta Q = 0$

*Assuming a mono-atomic ideal gas

9.3.1.4 Reversible and Irreversible Processes in Thermodynamics

Most laws of physics do not depend on the direction of time. For example, if you watched a video clip of a billiard ball collision (and could not see anything else in the video), you might have a difficult time telling if the video was being played forward or backward. In other words, the laws governing the collision do not depend on the direction of time. As another example, the Moon orbiting the Earth looks the same either forward or reversed. The laws of attraction and motion work for either direction of orbit and are physically indistinguishable.

However, we know that some processes cannot be reversed. For example, a snowflake lands on your hand and melts. This process never happens in the reverse direction *on its own*. As another example, a deck of cards falling off of a table cannot go in reverse on its own (the scattered cards will not restack themselves on a table.) Or even more unlikely, drop a deck of cards and they "randomly" reshuffle into the perfect poker hand. Consider a car skidding to a stop. Where does the kinetic energy of the car go? The skidding of the tires will heat the tires and pavement. But we know that this process will never spontaneously evolve in reverse. In other words, the reverse process—a car accelerating from rest (but the tires are not rotating) and leaving the road surface colder—*does not naturally happen*.

Natural processes such as these tend to move toward a greater disorder. Anytime there is friction, dissipating other forms of energy into heat energy, or if there is heat transfer from hot to cold, the process is *irreversible*. Dropping and breaking a dish is an irreversible process and illustrates nature's tendency toward increasing disorder. A broken plate on the floor has the same energy as an unbroken plate: same energy but one has greater disorder in the system. As a final example of this process, if we put lukewarm beer in a cooler full of ice, we would never expect the beer to become warmer and the ice to become colder. It is important to underscore that all of the above processes do not violate the first law of thermodynamics, the conservation of energy. So, we need another rule that somehow measures the ways energy can be distributed in a system.

All of the above processes could be reversed, but at great expense. We could build a device that will warm the beer and make ice colder, or we could repair the broken plate, but this will require energy and effort from the outside world. All we are saying is that nature does not do these things spontaneously. It turns out that there is another state variable that measures the number of ways energy can be distributed (ordered or not) in a system. It is called *entropy* (S). Just as with the internal energy of a system, the total amount of entropy in a system does not matter so much as the changes in entropy in the system. The change in entropy of a system is defined as the amount of heat energy delivered at constant temperature,

$$\Delta S = \frac{\delta Q}{T}. \tag{9.12}$$

Entropy is often tied to the "degree of disorder" of a system or the dispersion of internal energy. The more ways energy can be distributed within internal macrostates of a system, the higher the entropy. Let us consider a basket of tennis balls. If we pour the balls out of the basket, the balls tend to disperse. This analogy is applicable to the diffusion of thermal energy. Consider the warm beer in the ice cooler. As the heat leaves the beer and warms the ice, the heat energy is dispersed among the total contents of the cooler—the entropy of the total system is increasing.

We can use the beer and ice example to show how entropy changes using the above definition. Let us assume that we have 5 kg of ice at 0 °C (273 K, 32 °F) and 5 kg of beer initially at 40 °C (313 K). We put both into a very well insulated cooler. We can then calculate (a) how much ice is left and (b) the entropy change of the beer, ice, and the system. We start by assuming that there is enough ice that the final temperature will be 0 °C and find the amount of heat required to cool the beer. The amount of heat to be removed from the beer is:

$$\delta Q = 5\,\text{kg} \times 4181 \frac{\text{J}}{\text{kgK}} \times (-40\,\text{K}) = -836{,}200\,\text{J}, \tag{9.13}$$

This means that 836,200 J of energy must be added to the ice. Considering the latent heat of fusion for water (334 k J/K), the energy required to melt 5 kg of ice at 0 °C is:

$$Q = 334{,}000 \frac{\text{J}}{\text{K}} \times 5\,\text{kg} = 1{,}670{,}000\,\text{J}, \tag{9.14}$$

so there is enough ice.

CHECKPOINT 9.7
How much ice of the original 5 kg melted into water and how much remains as ice?

The entropy change of the ice is straightforward to calculate since melting occurs isothermally. The change in entropy is positive since the ice gained thermal energy:

$$\Delta S = \frac{836{,}200\ \text{J}}{273\ \text{K}} = 3063\ \text{J/K}. \tag{9.15}$$

The entropy change of the beer is a bit more difficult to find since the temperature was not constant. This will take a bit of calculus to show the details, but the final result is useful. Starting with

$$\Delta S = \frac{\delta Q}{T} = \frac{mc \cdot \Delta T}{T}, \tag{9.16}$$

with c the specific heat and m the mass. Approaching the Δ's as small differentials,

$$\Delta S = \int_{Ti}^{Tf} \frac{mc \cdot \mathrm{d}T}{T} = mc\ \ln\left(\frac{T_f}{T_i}\right). \tag{9.17}$$

So, the entropy change for the beer is:

$$\Delta S = 5\,\text{kg} \cdot 4181\,\frac{\text{J}}{\text{kg} \cdot \text{K}} \ln\left(\frac{273}{313}\right) = -2858\,\text{J/K}. \tag{9.18}$$

We note that the entropy change for the ice is greater since it absorbed the same heat energy as the beer lost, but at lower (smaller) temperature. Also note that the *total entropy change for the system* is +205 J/K. As mentioned before, this process is irreversible; we never see beer getting warmer and ice getting colder in a closed system on its own. Although energy is conserved (the net change in energy is zero!), entropy has increased as it will always for isolated, irreversible processes.

We are now in a position to state the second law of thermodynamics in a variety of forms. The Clausius statement (after the German scientist Rudolf Clausius) of the second law is:

> No process is possible who sole result is the transfer of heat from a colder to a hotter body.

An equivalent form of the second law due to Lord Kelvin is:

> No process is possible whose sole result is to transfer a quantity of heat from a body and convert it entirely to work,

which is the same as taking unorganized heat energy and making a more organized energy in the form of work. Notice the words, "sole result." It is possible to move heat energy from a cold object to a warmer object, but this requires an input of work. These two statements are also equivalent to the Planck version of the second law:

> Every process occurring in nature proceeds in the sense in which the sum of the entropies of all bodies taking part in the process is increased. In the limit, i.e. for reversible processes, the sum of the entropies remains unchanged.

This essentially means that $\Delta S_{\text{system}} \geq 0$ with the equal sign applying to reversible process. This implies that energy spontaneously disperses from being localized to becoming spread out if it is not hindered from doing so.

9.3.1.5 The Most Efficient Cycle: The Carnot Cycle

We will consider another cycle before tackling the refrigerator. The *Carnot heat engine* is a four-step cycle where we extract work in exchange for heat. It is another theoretical construct, and our assumptions and the processes in the cycle are such that all steps are reversible. This cycle is important since it determines the absolute theoretical maximum efficiency that is possible within the constraints of the laws of thermodynamics. We will use the example piston and cylinder again. The Carnot cycle has two isothermal processes which are assumed to occur "slowly," so the gas in the cylinder is always in thermal equilibrium. The cycle also has two *adiabatic* processes. An adiabatic process is one in which the gas absorbs no heat energy. In other words, if we are compressing or expanding the gas, we assume that the walls of the cylinder are so well insulated that no heat enters or leaves the system; $\delta Q = 0$. Another way of saying this, an adiabatic process occurs so quickly that the system does not have time to absorb or release heat. This then implies, from the first law of thermodynamics, that $\Delta U = -\delta W$. It turns out that the pressure and volume for this process are related by:

$$PV^{\gamma} = \text{constant} = K. \tag{9.19}$$

where $\gamma = C_P/C_V$. The work done during an adiabatic process is calculated by integrating this over the change in volume; the result of this integration is the equation shown in Table 9.4.

We will assume that the adiabatic process happens in such a way that it is reversible. A *reversible* adiabatic process is also known as an *isentropic* process, where the change in entropy is zero ($\Delta S = 0$).

Using the *PV* diagram shown in Fig. 9.12, the four steps in a Carnot cycle are as follows:

- **Isothermal expansion** The working gas is allowed to absorb heat Q_H from a hot object isothermally. During this step, the gas does work on the environment. There is positive work on the environment, and the change in entropy for this step is $\Delta S_1 = Q_H/T_H$.
- **Isentropic expansion** No heat energy enters or leaves the gas during this step. Since this is an expansion (volume increases), the temperature decreases to the temperature of the colder object. Considering that this is an expansion ($V_f > V_i$) and looking at the area under the curve, additional positive work is done on the environment.

- **Isothermal compression** Starting with this step, the environment does work on the gas, compressing it. It is assumed that the gas is always in thermal equilibrium with the colder object and heat Q_C is transferred. The change in entropy for this step is $\Delta S_2 = Q_C/T_C$ and is the same as ΔS_1.
- **Isentropic compression** Again no heat energy enters or leaves the gas in this step. Since this is a compression, the temperature of the gas increases to that of the hot reservoir. Just like step 3, there is negative work done by the gas on the environment.

At the end of the cycle, there is a net positive amount of work done on the environment. The work done is the area of the squashed "rectangle" enclosed by the paths drawn in the PV diagram shown in Fig. 9.14.

Carnot was able to show that this cycle has the maximum possible efficiency under the restrictions of the second law of thermodynamics. The efficiency of such a heat engine is given by the equation:

$$\begin{aligned} \eta &= \frac{W}{Q_{\text{in}}} \\ &= 1 - \frac{T_C}{T_H} \end{aligned}, \tag{9.20}$$

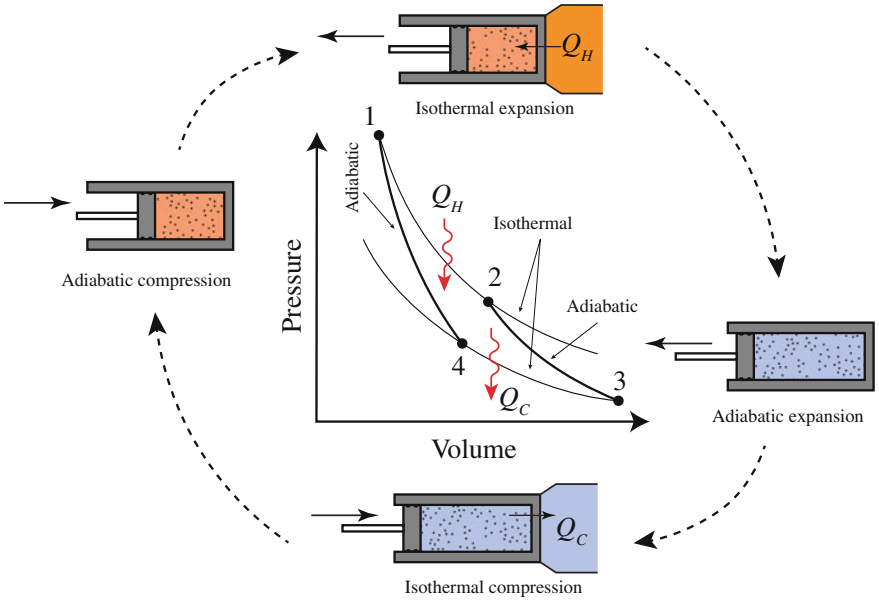

Fig. 9.14 Carnot cycle (heat engine) on a PV diagram

where

T_H is the temperature of the hot object and
T_C is the temperature of the cold object.

CHECKPOINT 9.8
What is the efficiency of a Carnot heat engine when the temperature of the hot and cold objects is the same temperature? What temperatures would you choose to maximize efficiency?

The Carnot cycle is completely reversible. To illustrate this, let us consider the above steps, but in reverse. Now, the environment does work on the system (or the system does negative work on the environment), and we are moving heat energy from the colder object to the hotter object. This is the same process that needs to occur in a refrigerator; heat is moved out of the cold interior of the refrigerator and moved to the outside of the refrigerator where it is hot already. Using the PV diagram shown in Fig. 9.15, the four steps in a Carnot refrigeration cycle are as follows:

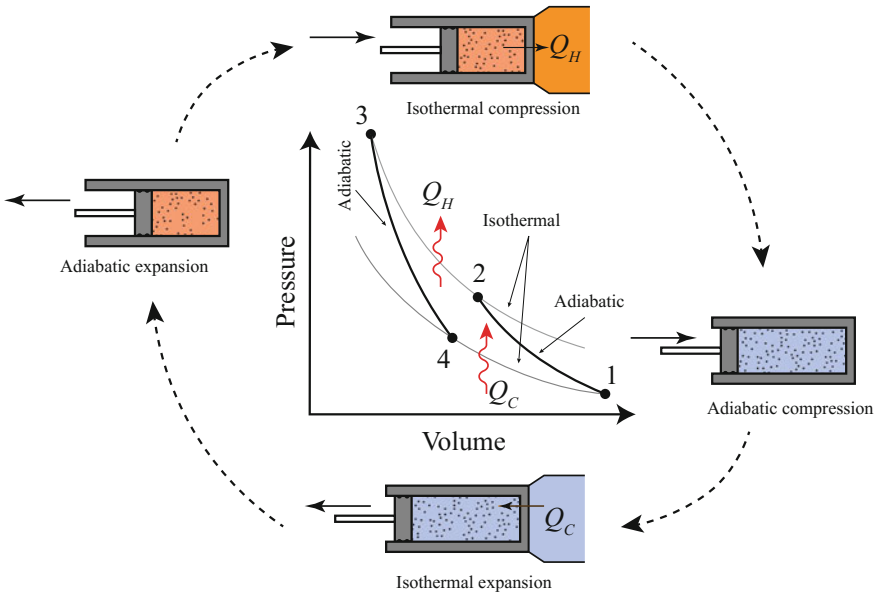

Fig. 9.15 Carnot refrigeration cycle on a PV diagram. Note that the starting point has changed from Fig. 9.14

- Starting from the bottom of Fig. 9.15 at point 1, **isentropic compression**. No heat energy enters or leaves the gas. Since this is a compression, the temperature increases to the temperature of the hotter object.
- **Isothermal compression** Now, the environment does work on the gas, compressing it. It is assumed that the gas is always in thermal equilibrium with the hotter object and heat Q_{H} is transferred.
- **Isentropic expansion** Again, no heat energy enters or leaves the gas. Since this is an expansion, the temperature of the gas decreases to that of the hot reservoir.
- **Isothermal expansion** The working gas is allowed to absorb heat Q_{C} from a cold object isothermally.

Since these processes are either constant temperature or constant entropy, it is more convenient to illustrate the process on a temperature–entropy (T–S) diagram, as in Fig. 9.16, instead of a P–V diagram.

Using the notion of efficiency, we can define a "coefficient of performance" (COP) for a refrigeration cycle by the ratio of "what you get" to "what you pay for" (see Fig. 9.17). What we get in a refrigeration system is an amount of heat Q_{C} removed, and we had to add in a certain amount of work. Since, by definition, work is defined as positive when work is done on the environment by the system, the COP is:

$$\mathrm{COP} = \frac{Q_{\mathrm{C}}}{-W}. \tag{9.21}$$

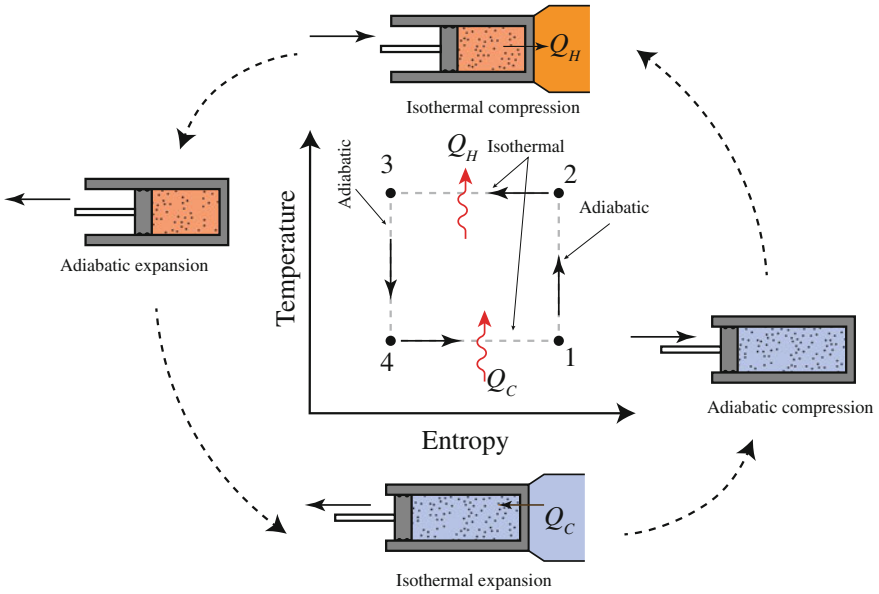

Fig. 9.16 Carnot refrigeration cycle on a TS diagram

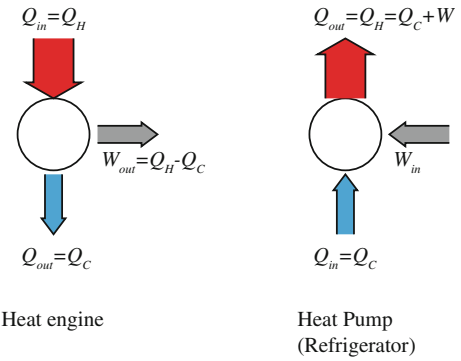

Fig. 9.17 Effective operation of a heat engine or refrigerator

Using the Carnot cycle, it can be shown that the maximum COP is given by:

$$\mathrm{COP} = \frac{T_\mathrm{H}}{T_\mathrm{H} - T_\mathrm{C}}, \tag{9.22}$$

which can be greater than one.

What steps do we need to do to implement the Carnot refrigeration cycle and use it to cool our beer? First, we need to find a process that absorbs or releases heat at constant temperature. Fortunately, when a substance changes from a liquid to a vapor, the temperature remains constant. (You can verify this by measuring the temperature of ice water as the ice is melting. It stays constant the entire time until all of the ice is gone.) The energy added to cause this change does not affect the temperature. Instead, it separates the molecules of the substance so that the liquid becomes vapor. The latent heat of vaporization is the value used to determine the amount of energy required to convert the liquid into vapor per unit of substance. So, for the isothermal processes, we just need to "boil" (evaporate) the fluid during the isothermal expansion (4 → 1) and "condense" the fluid in the isothermal compression (2 → 3). Physical implementation of isothermal heat transfer is easy with a heat exchanger.

Figure 9.18 shows a typical phase diagram for most substances, with the Carnot cycle superimposed. To the left of the bell-shaped curve, the fluid is a liquid, and to the right, it is a pure vapor. But at intermediate entropies inside the bell-shaped area, it is a mixture of liquid and vapor. We have placed the Carnot cycle in this area since we want the isothermal processes to just change the phase of the fluid. However, there are issues with actually implementing this for the compression and expansion phases. For instance, during the adiabatic compression (1 → 2 in Fig. 9.18), we would require a device that could handle both liquid and vapor at the same time. A compressor that can handle both phases would be relatively expensive. The same is true for the adiabatic expansion (3 → 4). We would require a device to extract work from the fluid, such as a turbine. Again, an extra device that could handle both phases would be impractical. So, we will make some compromises. First, we will use a free expansion for the adiabatic expansion portion. This

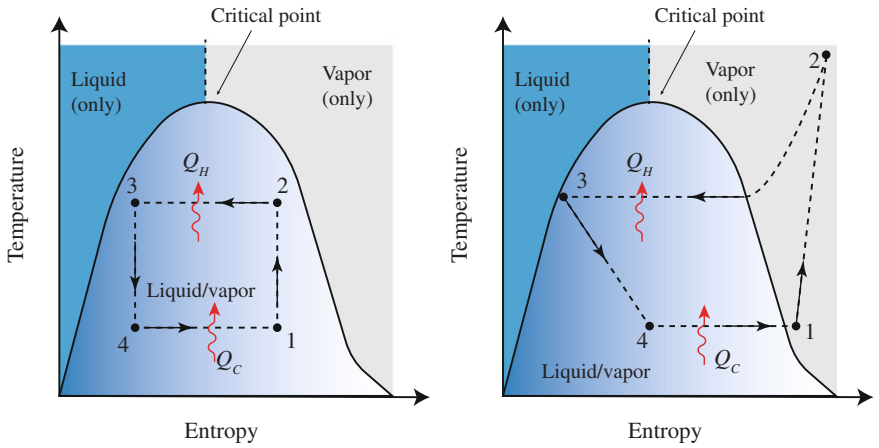

Fig. 9.18 *Left* ideal carnot refrigeration cycle. *Right* practical implementation

is easy, just let the working fluid flow through a restriction and expand into a lower pressure area. Unfortunately, this process is not reversible and therefore not isentropic, but it is mechanically simple and cheap. This modifies the cycle diagram slightly as shown in Fig. 9.18. Secondly, we design the system so that the isothermal expansion ("the boiling") completely converts the working fluid into a vapor. Then, we just need a relatively simple and inexpensive compressor that will only need to handle the gas phase of the working fluid. Again, this will modify the final cycle, but the solution is practical and easy to implement (Fig. 9.19).

When working with refrigeration cycles, it is convenient to work with another state variable known as enthalpy. *Enthalpy*, H, is thermodynamically equivalent to the heat content of the fluid. Rearranging the first law of thermodynamics, we get:

$$H = U + P\Delta V, \tag{9.23}$$

Enthalpy can be viewed as the energy needed to create our system in a certain state (the internal energy) plus push away the environment to make room for it (the work, $P\Delta V$ term). Specific enthalpy (h) is another useful term. It is simply the enthalpy divided by the mass of the liquid (in kg). So specific enthalpy has units of J/kg.

$$h = \frac{H}{m}. \tag{9.24}$$

The nice thing about working with enthalpies is that these values are already known for many different refrigerants. In this context, the state diagram for the working fluid is plotted on a pressure–enthalpy (P–H) diagram as in the example shown in Fig. 9.20.

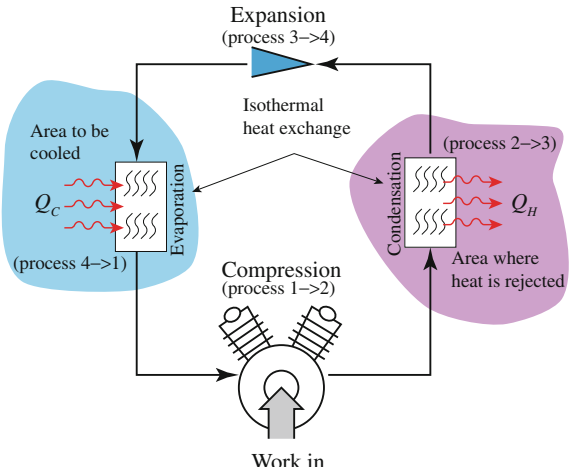

Fig. 9.19 Physical implementation of the approximate Carnot refrigeration cycle

A few words are in order for the P–H diagram. It is similar to the TS diagram in that the various states of the working fluid are separated: liquid, liquid and vapor, and just vapor. Looking at Fig. 9.20, the "tongue-shaped" curve represents the boundary for a saturated liquid on the left side and for a saturated vapor on the right side. The modified refrigeration cycle we discovered in Fig. 9.18 is also shown in the figure. We still consider the process $1 \rightarrow 2$ as an isentropic ($\Delta S = 0$) compression. However, we know that the expansion $3 \rightarrow 4$ is not isentropic because it is not reversible. But it is *isenthalpic* ($\Delta H = 0$) since there is no heat exchange with the environment. Also shown in the figure are representative lines of constant temperature (isotherms) and lines of constant entropy.

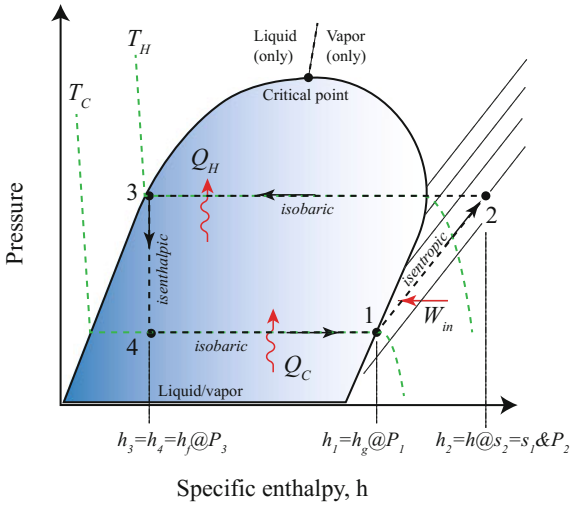

Fig. 9.20 Modified Carnot refrigeration cycle—the vapor compression cycle

The calculation of the rate of heat removal, or work done by the system, is fairly easy to calculate once each of the enthalpies is known. The *rate* that energy is exchanged with the system is commonly expressed in terms of the *rate* of mass flow:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}m}{\mathrm{d}t}(h_\mathrm{A} - h_\mathrm{B}). \tag{9.25}$$

using the change in specific enthalpy at two states A and B. Energy could be exchange of heat or work done depending on the process in question (Table 9.5).

Let us consider an example and calculate some values for our refrigerator. Consider a refrigeration cycle that uses the refrigerant 1,1,1,2-tetrafluoroethane (known as R-134a). It operates on the vapor compression cycle like that described above in Fig. 9.20. The high-pressure side of the cycle (process 2 → 3) is 0.9 MPa, and the refrigerant leaves the evaporator (at point 1) at −20 °C. If the mass flow rate of the refrigerant around the loop is 3 kg/s, what is (a) the rate of heat removal from the cold space, (b) the rate of heat rejection into the warm space, (c) the work input into the system, and (d) the COP of the refrigerator?

We start by looking up the specific enthalpies for R-134a from the data tables to describe each state.

- **State 1** The refrigerant is a *saturated vapor* at this point. We are given that the temperature is −20 °C. Looking at the data tables for R-134a in Appendix B, we find:
  - P_1 = 132.8 kPa.
  - $h_1 = h_\mathrm{g}$ at this pressure and temperature, so h_1 = 238.43 kJ/kg.
  - $s_1 = s_\mathrm{g}$ at this pressure and temperature, so s_1 = 0.9457 kJ/(kg K). We will need this for state 2.

- **State 2** The refrigerant is a *superheated vapor* at this point. But, since we assume that the process 1 → 2 is isentropic, we conclude:

Table 9.5 Summary of first and second laws applied to an ideal, closed vapor compression refrigeration cycle

Processes in Fig. 9.18	Components in Fig. 9.19	Process	Formulae
1 → 2	Compressor	ΔS = 0; (isentropic)	$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\mathrm{d}m}{\mathrm{d}t}(h_2 - h_1)$
2 → 3	Condenser	ΔP = 0; (isobaric and isothermal)	$\frac{\mathrm{d}Q_H}{\mathrm{d}t} = \frac{\mathrm{d}m}{\mathrm{d}t}(h_2 - h_3)$
3 → 4	Expansion	$\Delta H \cong 0$; (isenthalpic)	$h_3 = h_4$
4 → 1	Evaporator	ΔP = 0; (isobaric and isothermal)	$\frac{\mathrm{d}Q_C}{\mathrm{d}t} = \frac{\mathrm{d}m}{\mathrm{d}t}(h_1 - h_4)$

- $s_2 = s_1 = 0.9457$ kJ/(kg K).
- Now, we look up the enthalpy based on the pressure at this point and specific entropy. Since $P_2 = 900$ kPa is given in the statement of the problem and we now know s_2, we extrapolate from the data in Appendix B to get $h_2 \cong 276.3$ kJ/kg and $T_2 \cong 42.5$ °C

- **State 3** The working fluid is now a *saturated liquid*. At the pressure given, $P_3 = P_2 = 900$ kPa, we can get from the data table in Appendix B:

  - $T_3 = 35.5$ °C
  - $h_3 = h_f$ at this pressure and temperature, so $h_3 = 101.62$ kJ/kg

- **State 4** After the expansion, the refrigerant is a *mixture* of liquid and vapor at the lower temperature (−20 °C). Since the process is isenthalpic,

  - $h_4 = h_3 = 101.62$ kJ/kg

We are now in a position to calculate the requested information.

(a) the rate of heat removal from the cold space:

$$\frac{dQ_C}{dt} = \frac{dm}{dt}(h_1 - h_4)$$
$$\frac{dQ_C}{dt} = 3\frac{kg}{s}\left(238.43\,\frac{kJ}{kg} - 101.62\,\frac{kJ}{kg}\right) = 410.43\,\frac{kJ}{s} = 410.43\,kW$$

(b) the rate of heat rejection into the warm space:

$$\frac{dQ_H}{dt} = \frac{dm}{dt}(h_2 - h_3)$$
$$\frac{dQ_H}{dt} = 3\,\frac{kg}{s}\left(276.3\,\frac{kJ}{kg} - 101.62\,\frac{kJ}{kg}\right) = 524.04\,kW$$

(c) the work input into the system:

$$\frac{dW}{dt} = \frac{dm}{dt}(h_2 - h_1)$$
$$\frac{dW}{dt} = 3\,\frac{kg}{s}\left(276.3\,\frac{kJ}{kg} - 238.43\,\frac{kJ}{kg}\right) = 113.61\,kW$$

Note that we could have obtained this from $\frac{dW}{dt} = \frac{dQ_H}{dt} - \frac{dQ_C}{dt}$

(d) the COP of the refrigerator:

$$\text{COP} = \frac{Q_C/\text{d}t}{-W/\text{d}t}$$

$$\text{COP} = \frac{410.43\,\text{kW}}{113.61\,\text{kw}} = 3.61$$

CHECKPOINT 9.9
Using the temperatures in the example, calculate the theoretical maximum COP assuming a Carnot cycle.

9.3.1.6 Type of Refrigerants

The working fluid in a refrigerator needs to have a high latent heat of vaporization and a boiling temperature near the lowest temperature expected. Early refrigerants used ammonia, sulfur dioxide, methyl chloride, or propane. These substances are either extremely toxic or flammable and no longer widely used. The first "safe" refrigerant was invented in 1928 and marketed under the trade name Freon (R-12). This substance is a chlorofluorocarbon (CFC). It was discovered that when CFCs were released into the atmosphere, they generated free chlorine atoms (chlorine radicals). This has a serious detrimental effect to the ozone layer protecting the Earth. Newer versions of refrigerants are hydrogenated CFCs (HCFC), such as R-22 and R-123, or hydrofluorocarbons (HFC) such as R-134a. These compounds tend not to release chlorine atoms as readily as the CFCs, but it has been recently recognized that these gases are significant greenhouse gases. Greenhouse gases, in essence, reflect the heat generated by the Earth back to the surface causing it to warm. Given these problems, US manufacture of CFC-based refrigerants has been banned since 1996. Further, HCFCs are being phased out with an anticipated complete phase out by 2020. The search is on for a better refrigerant.

9.3.1.7 Mechanical Implementation of Refrigeration—Glycol Circulation

Closed-loop, vapor evaporation refrigeration systems tend to use refrigerants that are either toxic, harmful to the environment, or both if the working fluid is vented to the atmosphere. So, how do we cool our fermenters and other equipment? We need to be able to configure and reconfigure how the devices are being cooled in the brewery. Making and breaking connections with refrigerant in them is not possible (unless one is certified and using special equipment, it is against the law!). Also, who wants CFCs or ammonia accidentally getting into their beer?

The solution is to separate the working fluid of the refrigeration cycle by means of a glycol circulation system. Not that glycol is particularly healthy in beer if it accidentally goes in, but it does not pose the same environmental risks if it is

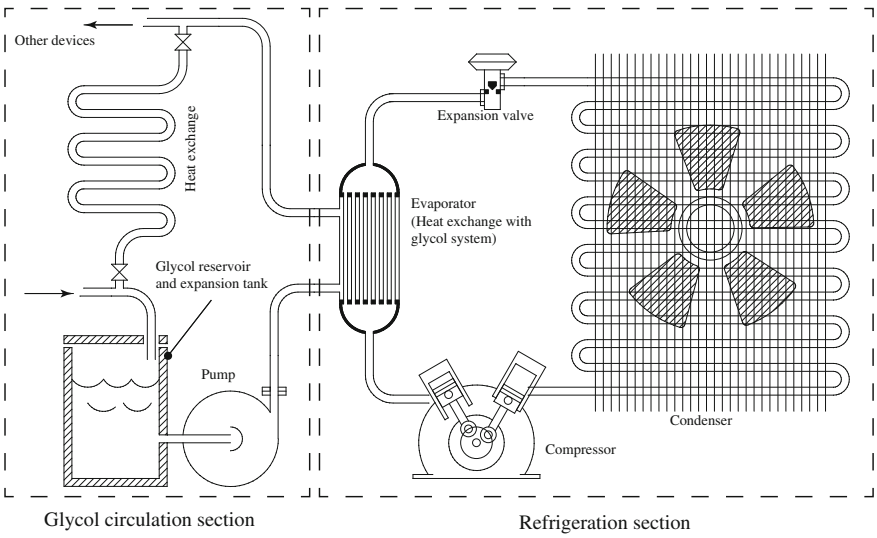

Fig. 9.21 Simplified glycol circulation-refrigeration system

accidentally spilled or released. Figure 9.21 shows a simplified glycol circulation system. A pump circulates glycol through a heat exchanger with the refrigeration cycle before it is pumped to the device(s) to be cooled.

This type of system is common in breweries, because the primary refrigerant can be contained in a particular area and the secondary coolant (glycol in this case) can be used throughout the brewery by simply pumping it in insulated pipes. The system only requires the addition of one refrigerator to the brewery instead of one for every fermenter.

9.3.2 Fermenters, CCV, and Round Squares

Early brewers used vats for fermentation. These vessels were open to the air and environment. But this was done because brewers did not understand that yeasts were needed to do the fermentation. Any attempt to ferment the wort in a closed vessel did not result in a good beer. Yeasts were added to these open vessels either by spontaneous fermentation (by the natural inoculation of yeast that happened to be floating in the air), by addition of *krausen* to the wort (krausen is the *barm* from another wort that was already actively fermenting), or by the inoculation of the wort using an *ale stick* or fermenting vessel that had previously been used to make beer. In the case of the ale stick, yeasts from an earlier batch that had become imbedded in the stick were able to start the fermentation. Ale sticks, in fact, were highly guarded family heirlooms that were passed from father to son. Loss of an ale stick was disastrous to the family that needed their beer.

As brewers' techniques improved, vessels were created not only to industrialize and standardize the brewing process, but to increase the efficiency and reduce the risk of contamination from unwanted microbes floating in the air. Many different styles of fermenter were explored. The more successful ones are discussed here.

Open/Square Fermenter One of the first fermenters used by brewers was open fermenters. Open fermenters are exactly what their name says they are. They do not have a top or cover. Although a lid can sometimes be added to them, it does not make a tight seal. Instead, if a lid is added, it is meant to keep things out, rather than keep things in. For example, the lid may be closed when a neighboring fermenter is being cleaned. The brewer adds the cooled wort to the open fermenter by splashing it into the vessel. This helps to aerate the wort.

Then, the yeast is *pitched* by simply pouring it into the vessel. If the vessel is rather large, it can be added as the wort is being added, so that the two mix together uniformly. Fermentation occurs, and a thick *barm* forms on top of the fermenting liquid. Barm is the name given to foam containing active yeast that rises above the liquid. If the brewer wishes to harvest the yeast off of the open fermenter, they can scrape off the layer of barm as it forms. The first scrapings are typically thrown away as they may be contaminated. The second scrapings go into a yeast *brink* to save for pitching the next batch.

The yeast brink is a small vessel that can hold suspended yeast. It typically has wheels or can be physically moved. The brink is stored in a refrigerator to keep the yeast cold or has a connection to a glycol circulation-refrigeration system. A manual stirrer is usually placed into the brink to keep the yeast suspended. In some cases, the brewer may wash the yeast to remove unwanted wort or reduce the number of unwanted bacteria. Washing can be done with high-quality liquor or with acidic liquor (typically a solution of phosphoric acid in water). The yeast can survive fairly low pHs for a short time, where the bacteria cannot.

Fermentation in an open container results in an un-carbonated green beer. Conditioning must still be performed. In addition, since the historical open fermenters did not have a built-in cooling or warming system, the fermentation typically took place at the temperature of the room. Modern open fermenters are usually square or rectangular in shape, are jacketed so that they can be cooled as needed, and are only 1–2 m deep. This allows the regulation of the temperature without much input from a glycol circulation-refrigeration system. In addition, the shallow depth to the fermenter increases the amount of esters and other flavors produced by the yeast (compared to deep fermenters that are greater than 2 m deep.).

Yorkshire Square The Yorkshire square was likely invented by Timothy Bentley (1768–1830) around 1795 when he opened the Lockwood Brewery near the present-day town of Huddersfield, West Yorkshire, England. This vessel was originally constructed from sandstone, but slate eventually became the norm. The stone was cut into panels and arranged into a double-decker square box pattern (Fig. 9.22). The bottom vessel was double-walled with a space between the walls to allow water to pass. The water was circulated through the gap so that the temperature of the square could be maintained.

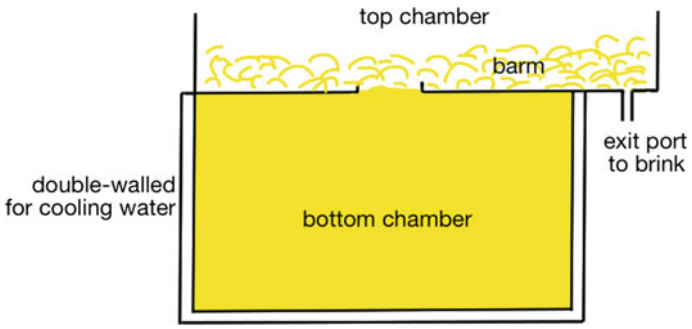

Fig. 9.22 Traditional Yorkshire square design

Yeast is pitched into the wort in the bottom vessel of the square. As it ferments, the yeast barm rises through the manhole in the center of the top deck. Here, the barm settles and the yeast can be harvested. Periodically, the yeast is *roused* by pumping it up to the top vessel and spraying it through a fan-shaped sprayer to mix with the yeast. This stirs the yeast and increases the rate of fermentation. Then, the manhole is opened and the slurry splashes back into the bottom vessel. This process can be repeated a couple of times until the wort is nearly free of sugars. At this point, the beer can be transferred into casks or kegs to finish the fermentation and carbonate the beer. The yeast can be harvested from the top vessel after the wort has been returned to the bottom half of the vessel.

This system of fermentation experienced widespread use in parts of England. However, development of new methods and processes has resulted in the replacement of this fermenter with other technology. A few breweries still use the Yorkshire square, but they tend to have only a cult following. Due to problems that include cleaning the lower chamber, modern squares tend to be made from stainless steel with a jacketed lower chamber. These modern systems (known as "round squares") also tend to be round in shape to aid with cleaning.

Double drop The issues with the Yorkshire square design led to the development of the double-drop system for fermentation in the late 1800s. In this system, the cooled wort was pumped (or "dropped") into a fermenter. The action of pumping the wort splashed it with air and helped to add oxygen to the wort. About 14 h after pitching the yeast, the actively fermenting wort was dropped by gravity into another fermenter with splashing and allowed to finish fermentation. The process removed the actively fermenting wort away from remaining trub and dead yeast, resulting in a cleaner fermentation and clearer beer.

This system is not extremely common today, but has found use in many breweries. The second drop was performed to re-aerate the wort and encourage further yeast growth, much like the rousing that is done in the Yorkshire square system. And, just like the Yorkshire square system, the double drop causes the production of esters and other compounds that can contribute to the flavor of the beer.

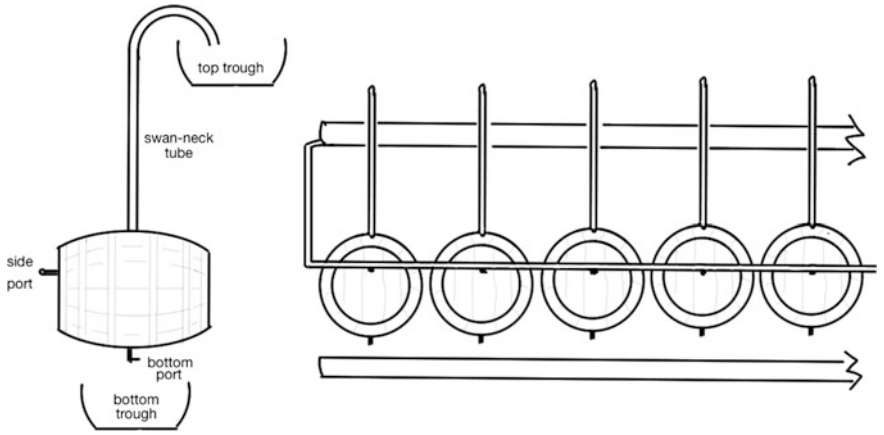

Fig. 9.23 Burton Union system. Barm rises through the gooseneck (or swan-neck) tube into the *top* trough. The liquid settles and is returned to the casks via the side port. Yeast remains in the *top* trough. Once complete, the beer is drained from the casks into the *bottom* trough where it runs to the conditioning tank for treatment and packaging

Burton Union The Burton Union system was created in the 1830s as a way to perform the same process as the Yorkshire square, but in more readily available wooden casks. This process involved pitching yeast into an open fermenter containing fresh wort. After 12–24 h, the actively fermenting wort was then fed by gravity into a series of wooden casks (Fig. 9.23). A gooseneck-shaped tube was then attached to the cask that ended in a trough above the casks. As the fermentation continued, the barm rose into the gooseneck and dropped into the trough. Here, it was separated, wort dripped back down into the casks, while much of the yeast remained behind in the trough.

This process clarifies the beer quickly. Remaining trub and dead yeast are retained in the original fermenter, and as the yeast are pushed through the goosenecks in the wooden cask fermenters, the amount of remaining un-dissolved solids in the beer are removed. Typically, after 6 days in the casks, the beer is moved to a conditioning tank for carbonation, blending, or packaging.

Less than a handful of breweries in the world continue to use the Burton Union system. This is primarily due to the fact that the system requires constant care and maintenance. Cleaning between runs must be done with only hot water as chemicals and cleaners can damage the wood. In fact, Marston's Brewery in Wolverhampton, just northwest of Birmingham, England, holds fast to the use of this system. They believe that their mixture of yeast strains and the system provide a unique flavor profile for their beers that could not be obtained by other methods.

Cylindroconical Vessels (CCV) By far, the most common of the fermenters are the closed fermentation systems known as cylindroconical vessels (CCVs) or uni-tanks. These were an instant hit when they were invented and replaced many other fermentation systems. By the mid-1900s, they were well entrenched in the

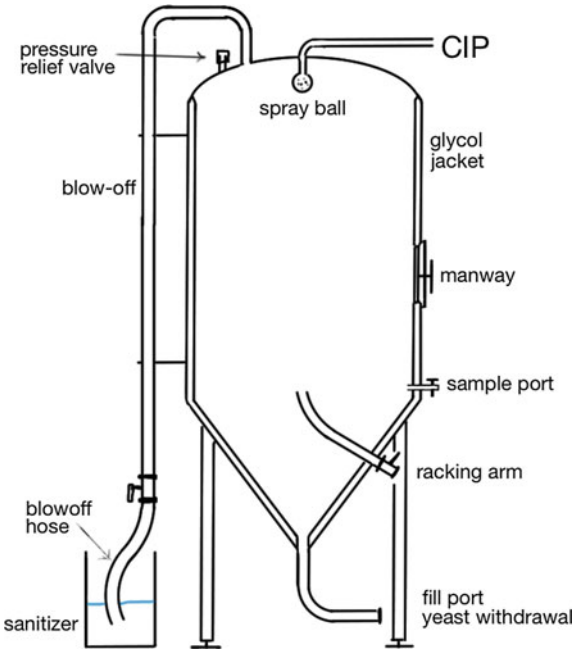

Fig. 9.24 The cylindroconical vessel (CCV). The blow-off tube is connected to a hose that is placed in a bucket of sanitizer. Bubbles of CO_2 can be seen exiting through the bucket. The racking arm is a tube that can be rotated to withdraw clear beer from the fermenter without transferring yeast. The *bottom* port serves as the fill port and the yeast withdrawal port. Zones within the glycol jacket allow different regions of the fermenter to be cooled

fermentation process. The vessels allow the fermentation process to be conducted at a slightly higher pressure (which allows the fermentation to proceed faster). In addition, the shape of the base of the vessel provides a way to remove any trub and dead yeast, or even harvest clean yeast. Because of this, the CCV can be used as the primary fermenter, secondary fermenter, and even the conditioning tank (hence the term uni-tank).

The vessel, shown in Fig. 9.24, is jacketed to allow the temperature of the wort inside to be controlled. Zones in the jacket along the sides and bottom of the vessel also provide additional control to the fermentation. During active fermentation, the yeasts rise through the center of the vessel and then cascade down along the side of the vessel where the yeasts are then deposited on the bottom. The slope of the bottom forces the yeast to collect in the cone. Then, by simply opening a valve, the brewer can collect it as needed.

The CCV also has a CIP ball in place to clean the interior of the vessel with limited labor. In fact, since computer servomotors can operate all of the valves, the use of the CCV helps automate the entire brewery. They are inexpensive, are easy to maintain, and occupy significantly less floor space than any of the open fermenters. With appropriate insulation, they can even be placed outside of the brewery. The larger of these fermenters can hold 6000 hL or more. The pressure on the yeast at the bottom of the fermenter limits the maximum size of the fermenter.

CHECKPOINT 9.10
Provide a drawing of a typical yeast brink. Plan how you would add the yeast from an open fermenter into the brink, and consider how the yeast could be pitched from the brink into another fermentation.

9.4 Yeast

Yeasts are single-celled microorganisms, classified as fungi. As we have already discovered, there are two major species of yeast that are useful in brewing (and many others that are not.) Those two species are *Saccharomyces cerevisiae* (aka ale yeast) and *Saccharomyces pastoranus* (aka lager yeast). Each of these species has a large number of variants or cultivars. Each of these cultivars has been developed based upon the desired final characteristics of the brewed beer. The characteristics actually define the cultivar and determine whether the particular yeast is suitable for a given style of beer. Often these are very proprietary. Breweries that develop a specific cultivar for one of their own brews tend to be very protective.

Yeasts are facultative anaerobes. This means that they are able to grow in the presence or absence of oxygen. The brewer uses this to their advantage. When they begin the fermentation process, they add oxygen to the wort. Under these aerobic conditions, the yeasts begin to grow, increasing their numbers until the oxygen has been consumed. Some carbon dioxide is also produced as they uptake fermentable sugars. At this point, their metabolism adjusts and they begin making ethanol and carbon dioxide. Eventually, the alcohol concentration gets too high or the amount of sugars still in solution gets too low, and the yeasts begin to come together and flocculate.

Brewers and microbiologists develop new yeast cultivars to enhance certain properties of the yeast as it goes through fermentation. Focus tends to be on the following key features.

Flocculation As yeasts enter dormancy during and at the end of the fermentation process, they flocculate. Proteins that extend from the surface of the yeast cell point outward when calcium binds to them. These proteins interact with those on neighboring yeast cells, again in the presence of calcium ions, and "stick" together. As the yeasts enter dormancy, they gather together and form a large mass, with each yeast cell stuck together. This mass gets large enough that the yeast cells cannot stay suspended in the fermenting beer. So they fall out of solution and collect at the bottom of the vessel. If the yeast flocculates too slowly, they will remain suspended in the beer after fermentation. This could result in a cloudy beer at the tap. If the yeast flocculates too quickly, they may not hang around in the beer long enough to convert all of the fermentable sugars into alcohol, or worse, that the yeast do not

remain suspended long enough to absorb any of the bad off-flavors that may have been produced during the fermentation.

Attenuation This is a term that is used to describe how much of the fermentable sugars are converted into alcohol. As yeasts conduct their reactions, not all of the sugars are used to make alcohol; some of the sugar is used for other things (as we will see later in this chapter). In addition, attenuation can also refer to the ability of the yeast to continue to ferment sugars until they are all gone. Some cultivars of yeast turn dormant when the concentration of sugar in the wort gets low.

Operation Temperature The optimum temperature for the yeast to thrive in the sugar solution is another of the features that can be selected for when new cultivars are prepared. The temperatures can be as low as 40 °F or as high as 78 °F (or even more separated than this). The temperature range for a cultivar determines whether that yeast will be used in creating a lager (low temperatures) or an ale (high temperatures).

Alcohol Tolerance Many yeast cultivars are fairly resistant to the presence of alcohol in the fermenting wort. Others are not so resistant. Alcohol is toxic to yeast. Just look at the ingredients on the hand sanitizer that you use. Some cultivars stay active and survive in high concentrations of alcohols before they flocculate. Others flocculate quickly. The range of alcohol concentrations can go from as low as about 5 % all the way to about 14 % (or even higher).

Yeasts are incredible creatures. They are small enough that the unaided eye cannot see them, but cause such significant changes to a batch of sugar water in very short order. They execute their changes by growing and reproducing into the millions per milliliter. It is the sheer number of these creatures that do the work. Let us look into the yeast cell a little closer to learn more about them.

9.4.1 Yeast Morphology

The typical brewer's yeast is roughly 5–10 μm (a μm is a micrometer and often listed as "microns") in diameter. Under the microscope, these tiny cells are somewhat visible. They lack color and because they're so small brewers often add a colorizing agent in order to see them better. The typical colorizing agent is methylene blue. This compound stains the cells and leaves the background wort in which the yeasts live slightly blue in color. The methylene blue stain also has another use (in addition to making the yeast visible). We will uncover that later in this section.

Yeasts have a cell wall connected to a membrane immediately inside the cell wall. The cell wall, which is about 25 nm (1 nm is 10–9 m), is 0.25–0.50 % of the entire distance across the cell. Even though it is relatively small, it makes up about 25 % of the dry weight of the cell. The cell wall contains regions that are primarily made up of different glucose polymers. The innermost region is almost entirely β-glucan. β-Glucan, in fact, is the major component of this and the middle regions

of the cell wall. However, at the innermost region, it is the sole component. As we uncovered earlier in this text, β-glucan is a structural molecule. It has linkages that are not easily broken, and the molecule adopts a very linear structure.

The middle of the cell wall is a region that contains some mannan interspersed in the β-glucan matrix. Mannan is a polymer of mannose with α-[1 → 6] linkages along the main chain of the polymer and branches with α-[1 → 2] and α-[1 → 3] linkages (see Fig. 9.25). In addition, this region of the cell wall contains some proteins.

The outermost region of the cell wall contains mostly proteins and enzymes. Many of these proteins have small chains of mannan or mannose bound to them. The enzymes in this region include invertase (an enzyme that hydrolyzes sucrose into glucose and fructose), β-glucanase and mannosidase (enzymes that can hydrolyze β-glucan and mannan into smaller pieces; likely, these enzymes help break down the cell wall during the growth stage of yeast) and lipase (which hydrolyzes fats and lipids). The proteins include flocculation protein 11 (aka FLO11), a calcium-binding protein that helps the yeast adhere to other yeast cells during flocculation.

The cell membrane is about 7.5 nm thick. It is made up of phospholipids, sphingolipids, and sterols. These molecules are relatively linear in their shape. At one end of these molecules are oxygen, nitrogen, and phosphorus atoms. The rest of the molecule tends to be carbon-based. The oxygen, nitrogen, and phosphorus atoms tend to form hydrogen bonds with molecules such as water or carbohydrates. These are polar molecules that interact with the polar end of the cell wall molecules. The long carbon chain region of the cell membrane molecules tend to be nonpolar in nature and do not interact with water or the cell wall very well.

The cell membrane sets up as two layers of these molecules (known as a lipid bilayer). The first layer is oriented so that the cell membrane molecules are oriented to the polar ends facing the cell wall. The second layer is oriented so that the polar ends of the molecules are oriented to the center of the yeast cell (Fig. 9.26). The cell membrane is fluid and moves around. Any molecules embedded in the membrane can then migrate along the cell membrane to where they are needed.

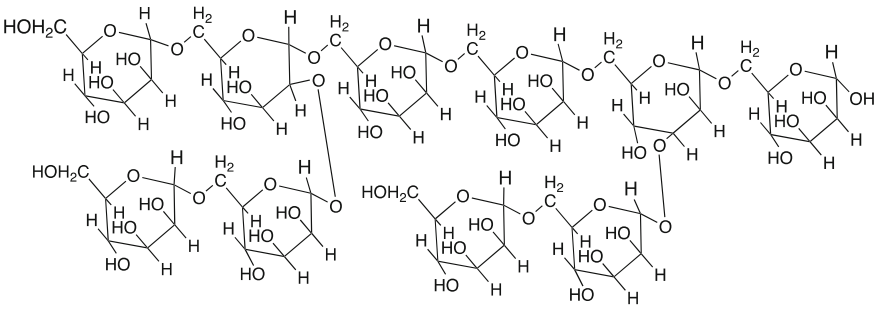

Fig. 9.25 The structure of mannan, a polymer of mannose. Note the similarities and differences to starch (Fig. 6.11)

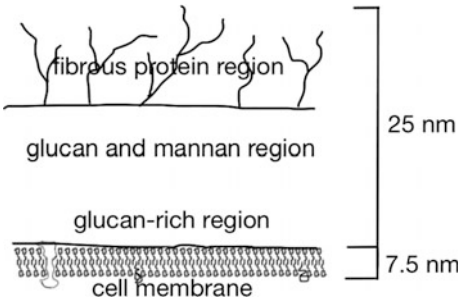

Fig. 9.26 Cell membrane

Inside the cell are a series of structures like organs in a human body. The nucleus is wrapped in a membrane. It contains the genetic material (DNA, RNA) that defines the makeup of the proteins, enzymes, and other materials that are made by the cell. Mitochondria also exist in the cell. These are the engine of the cell where enzymes convert sugars into energy. The endoplasmic reticulum, which is attached to the nucleus membrane, is the location where enzymes and proteins are produced. The vacuole can be thought of as a large sack. It serves as a storage vessel for sugars and other compounds that the cell needs as nutrients. Finally, lipid granules can also be found in the cell. These are essentially fat storage for long-term energy needs by the cell.

As the cell grows, it softens an area of the cell wall. Then, it makes more cell wall material and pushes out until a small bud is formed. The vacuole separates into a large number of smaller sacks. Some of these migrate to the bud in order to become the vacuole for the new yeast cell. The DNA duplicates itself, and the nucleus splits into two: One stays behind, while the other ends up in the bud. Finally, when all of the organs have been made, the cell wall pinches shut and the *daughter cell* is formed. The cell wall, however, is scarred during the process. Repair of the cell wall leaves a ring of chitin (a polymer of aminoglucose) in the cell wall. Similarly, the new daughter cell is marked with a *birth scar*. This hard polymer cannot be broken down. Thus, when the yeast has budded multiple times so that the entire surface of the cell is marked with *bud scars*, it cannot produce another bud. The entire process, in sufficient oxygen, takes 60–120 min.

9.4.2 Yeast Metabolism

Yeasts are pitched into the fermenter and become suspended in the sugary wort. We will recall that the wort at this stage is the perfect temperature for yeast to grow and is laden with fermentable sugars, amino acids, and other nutrients that the yeasts need to grow. In addition, the wort is fully oxygenated with approximately 8–10 ppm oxygen. The yeasts at this point begin to grow, and while the oxygen is present, they enter something we call aerobic metabolism. Aerobic conditions indicate the presence of oxygen.

The yeasts absorb oxygen in the solution as they grow. This depletes the concentration of oxygen in the solution. So, after some rapid growth, the yeasts have eliminated all of the oxygen in the solution. This triggers the yeast to enter anaerobic metabolism. Under anaerobic conditions (conditions where oxygen does not exist), the yeasts continue to consume fermentable sugars but convert them into ethanol and carbon dioxide.

9.4.2.1 Aerobic Conditions

Aerobic conditions refer to the presence of oxygen in the medium. In these conditions, the yeasts take up the fermentable sugars in the solution. Those sugars include glucose, maltose, and maltotriose. In some cases, the brewer may have added sugar to the wort. In the first steps, the yeasts utilize the sucrose through the action of the invertase that is found outside of the cell wall. Invertase hydrolyzes sucrose into glucose and fructose. It has been found that glucose is the first carbohydrate to be taken up by the cell at a rate twice as fast as fructose. Then, fructose, maltose, and maltotriose in that order are consumed. There is some overlap to their rates of uptake.

Once inside the cell, a special hydrolase (enzyme that adds water across a bond) converts maltose into two molecules of glucose. Similarly, maltotriose is broken down into three molecules of glucose.

Glucose is metabolized via glycolysis. This is a pathway that converts glucose into small building blocks that can be used to make other molecules that the yeasts need to grow. Figure 9.27 outlines each of the steps in glycolysis. The first step is to add a phosphate group to the molecule to improve solubility. The second step converts the glucose molecule into a fructose molecule. Another phosphate group is added to make fructose-1,6-diphosphate. This molecule is cleaved into two three-carbon pieces (glyceraldehyde 3-phosphate and dihydroxyacetone phosphate). These two pieces can be converted into one another as needed. The glyceraldehyde 3-phosphate is oxidized over the next two steps to make 3-phosphoglycerate. The phosphate is then moved to the 2 position and then removed with oxidation to end up with pyruvate. If we look through the steps, we can see that one glucose molecule ends up making two pyruvates.

Along the way, high-energy molecules are used to drive the reaction forward. The high-energy molecules are known as adenosine triphosphate (ATP). When they release their energy, they form a molecule of adenosine diphosphate (ADP). Later in the glycolysis, the phosphates in the small molecules are removed and ADP is returned to ATP. One step indicates that a molecule of NAD+ is converted into NADH. In this step, electrons from NAD+ are used to oxidize the molecule of glyceraldehyde 3-phosphate. This step requires that adequate NAD+ be available, and if it is not, glycolysis shuts down entirely. Oxygen can create more NAD+ in order to keep this pathway going; however, when oxygen is scarce (as we will see below), the NAD+ has to be made from other sources.

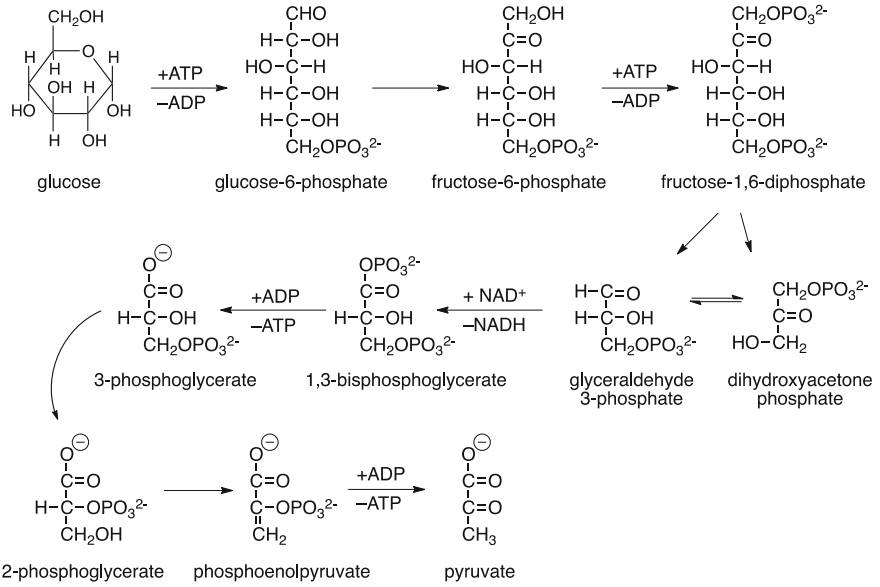

Fig. 9.27 Glycolysis. The input is glucose, and the outcome is two molecules of pyruvate

CHECKPOINT 9.11
What is the net change of ATP in the glycolysis of one molecule of glucose? How many NADH molecules are formed?

At this stage, the pyruvate can continue on to provide more energy and other starting materials for the synthesis of the molecules that the cell needs to survive. In order for it to move forward, however, it must be oxidized. This is a single step that converts pyruvate into acetyl CoA. Acetyl CoA is the shorthand for acetyl coenzyme A, a fairly complex looking molecule. However, the end of the molecule (the two atoms in blue in Fig. 9.28) contains the atoms from pyruvate.

Now, the molecule is ready for the next step, the citric acid cycle. This cycle moves molecules around generating energy and carbon dioxide along the way. Any of the molecules can be removed from the cycle to make amino acids or other compounds useful for the cell. Note that another molecule of NAD+ is reduced to NADH in this step.

The citric acid cycle (aka the Krebs cycle; shown in Fig. 9.29) begins where the acetyl CoA joins the process. If we color two atoms from acetyl CoA blue and follow them around the cycle, we can see that they are not eliminated in the first cycle. But in the second cycle, they can be. Note that succinate is a symmetrical molecule. That means the molecule can be flipped as it moves along to make

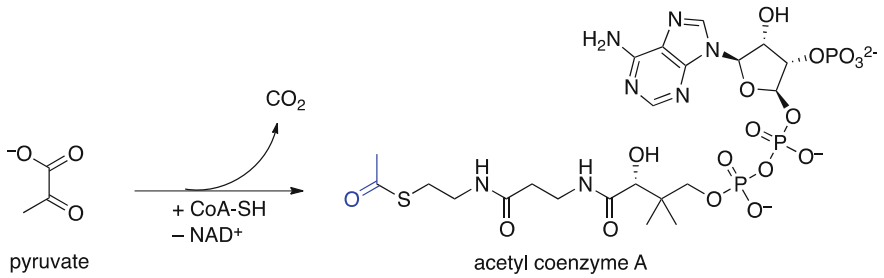

Fig. 9.28 Oxidation of pyruvate to provide acetyl CoA. The two carbon atoms from pyruvate end up on the end of the acetyl CoA

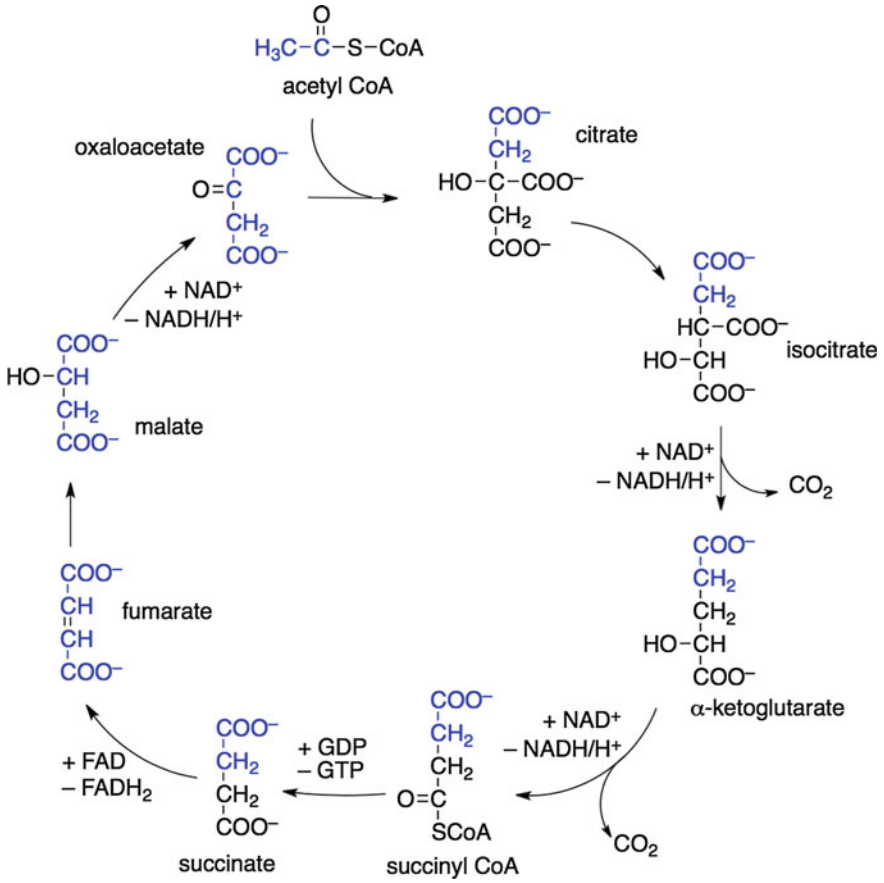

Fig. 9.29 Citric acid cycle. The two atoms from acetyl CoA are noted in *blue*

fumarate. Thus, at this step, the carbons from the original acetyl CoA get distributed among all of the atoms of the fumarate molecule.

This cycle consumes three molecules of NAD^+ and one molecule of FAD^+ (a compound that also transfers electrons like NAD^+). In addition, this cycle forms one molecule of GTP (guanosine triphosphate) which is similar in structure and function to ATP. In other words, a lot of energy is used up in this cycle. So, what's the benefit to doing the cycle? That is the next step in the process.

Oxidative phosphorylation is the last step in cellular respiration. It occurs on the inner membrane of the mitochondria. Here, NADH and $FADH_2$ donate electrons to large proteins that are embedded in the membrane. These proteins pass the electrons to the next protein in the chain. In addition, the protons (H+) that are formed in the redox reaction are pushed across the inner membrane of the mitochondria and into a space between the membrane and the outer membrane. The electrons eventually are delivered to molecular oxygen (O_2) to make water. The NADH and $FADH_2$ become NAD^+ and FAD^+ in the process. The large concentration of protons just across the inner membrane represents a very-high-energy state because anything in high concentration tends to move to the areas of low concentration (this is an entropy-driven process). As the protons move back across the membrane, they pass through an enzyme known as ATP synthase that converts ADP into ATP. The end result is the production of 30–32 ATP molecules for every molecule of glucose that the cell consumes. This represents a tremendous amount of stored energy that can be obtained from one molecule.

9.4.2.2 Anaerobic Conditions

However, the yeast cells do not have enough oxygen to continue to use the glycolysis–citric acid cycle–oxidative phosphorylation pathway forever. In fact, while glycolysis and the citric acid cycle can still be used (they do not require oxygen), only glycolysis and a portion of the citric acid cycle are truly available. When oxygen is low, the cell enters anaerobic metabolism and obtains energy from a different pathway.

That pathway is known as fermentation. In fermentation, some of the pyruvate made from glycolysis is used to make acetaldehyde by decarboxylation (Fig. 9.30). A molecule of NADH then reduces the acetaldehyde to ethanol and generates NAD^+ in the process. This also helps eliminate some of the acid (protons, H^+) generated in the cell during the consumption of sugars. In addition, the NAD^+ can be used by the cell to create additional ATP during the glycolysis steps. It is not a lot of energy compared to oxidative phosphorylation, but it is enough to keep the cell living.

Lactobacillus and Pediococcus can also ferment sugars. The pyruvate that they make after glycolysis, however, is reduced directly rather than becoming decarboxylated into acetaldehyde before being reduced. The result is the formation of lactic acid ($CH_3CHOHCOOH$).

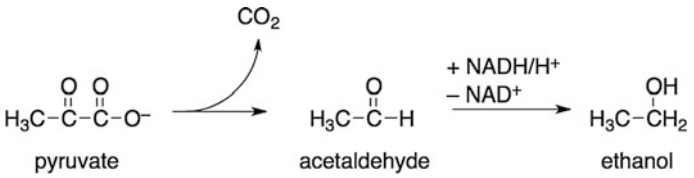

Fig. 9.30 Fermentation pathway in yeast

9.4.2.3 Effects on Metabolism

Two actions that brewers often perform have a measureable effect on the action of yeast. The first of these is known as the *Crabtree Effect*, named after Herbert Crabtree who explained it in the 1920s. In the presence of high concentrations of glucose, even under aerobic conditions, yeasts ferment and produce ethanol and carbon dioxide. This effect arises because the large concentration of glucose forces the production of a tremendous number of ATP molecules. Proceeding through the citric acid cycle and oxidative phosphorylation is not necessary. The result is that the yeast growth is slowed or stunted because the glucose is moved exclusively toward ethanol production.

The other effect is known as the *Pasteur Effect*, reported by Louis Pasteur in 1857. In the presence of oxygen, yeast growth is highly favored and fermentation is slowed or stopped. This effect arises because the presence of oxygen allows the yeast to use oxidative phosphorylation to obtain tremendous amounts of energy. So, if a brewer aerates their actively fermenting wort, the yeasts stop fermentation and multiply. This is exactly what happens when yeasts are roused or dropped in many of the fermentation systems. This effect can be beneficial if the number of yeasts in the beer is limited, but definitely not beneficial in the opposite case.

9.4.3 Products of Yeast

With all of the steps in the metabolism of sugars, there are a lot of different molecules that yeasts make. Just looking at the figures above, we can see common molecules such as citrate, acetyl CoA, ethanol, acetaldehyde, and oxaloacetate. Some of these are final products that are not further modified. Others are highly modified to form other compounds.

Esters are one class of compounds that are prized by brewers and produced by yeast during their metabolism of sugars. Research is still carried out on exactly how these form during yeast metabolism, but conjecture suggests that acetyl CoA plays a large role in making esters. An enzyme known as alcohol acetyl transferase (AAT) can catalyze the addition of an alcohol to an acetyl group from acetyl CoA. This type of ester is the most abundant in yeast fermentation. With restricted growth (low oxygen levels), the acetyl CoA is in abundance and can add to ethanol, butanol, and other alcohols found inside the cell.

Fatty acids are molecules containing the carboxylic acid group that has very long carbon chains attached. These molecules are used to make cell membranes, but sometimes can be esterified instead.

Fusel alcohols, alcohols other than ethanol that are present inside the yeast cell, are made from α-ketoacids. The α-ketoacids are by-products and intermediates in the synthesis of amino acids. In fact, it has been shown that a yeast strain deficient in its ability to make valine and isoleucine (two amino acids) was unable to prepare 2-butanol, 3-methyl-2-butanol, and 2-pentanol. Thus, these alcohols come about as the yeast cell is undergoing rapid growth and producing large quantities of amino acids for the new yeast cells.

Diacetyl and other VDKs are produced during rapid growth as well. Diacetyl itself comes from valine production, specifically from α-acetolactate, a precursor to the formation of the amino acid (Fig. 9.31). The biosynthesis of valine involves four separate steps from pyruvate. Once the α-acetolactate is excreted from the cell, it undergoes a spontaneous oxidative decarboxylation to produce diacetyl. This step requires, as we have discovered previously in this text, the presence of metal cations or oxygen in order to work.

Yeasts then slowly uptake diacetyl and other VDKs when the concentration of fermentable sugars is low. Once back inside the cell, diacetyl is reduced by NADH forming NAD^+ and acetoin ($CH_3CHOHCOCH_3$). The NAD^+ is used by the cell (see the figures above). Acetoin is further reduced to 2,3-butanediol by another NADH, resulting in the total production of two molecules of NAD^+ for every molecule of diacetyl.

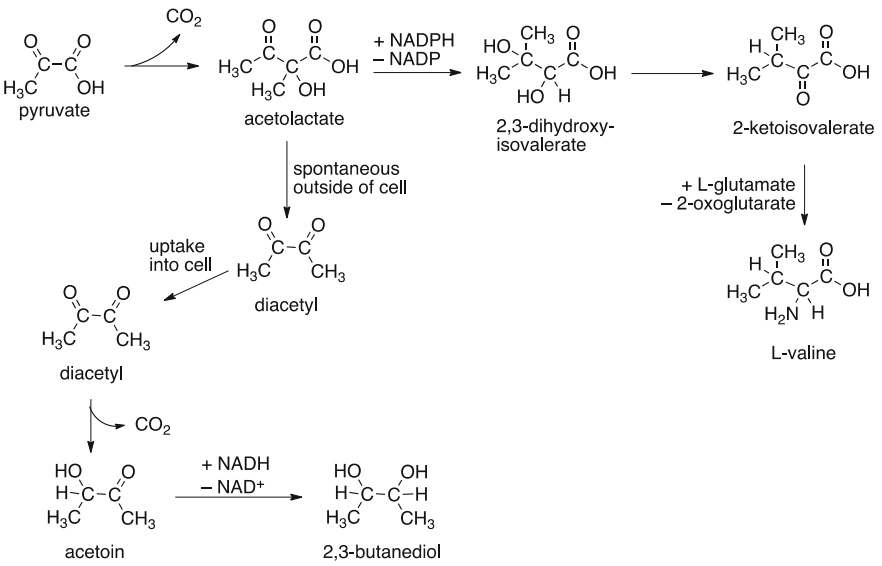

Fig. 9.31 Production and uptake of diacetyl

Each of these molecules would be undetectable in beer if they stayed inside of the cell walls. However, large quantities of them produced inside the cells either can leak through the cell walls or can be transported outside of the cell as waste products. Carbon dioxide, for example, is a small molecule that simply diffuses across the cell wall. Acid (i.e., protons, H+) is transported using specialized cellular pores. In the end, if it is inside the yeast cell, it likely will leak out and flavor the beer.

Chapter Summary

Section 9.1

Fourier heat equation can be used to determine the rate of heat transfer.
Wort can be cooled using the shell and tube and the plate heat exchangers.

Section 9.2

The ideal gas equation relates the pressure, temperature, amount, and volume of a gas.
The amount of work done by or on a system can be calculated from equations based on the type of process.
Pressure–enthalpy diagrams can provide information about a refrigeration process.
Glycol refrigeration systems are used to cool equipment and vessels in a brewery.
Fermentation vessels include open and closed systems. The CCV is the most common of the fermenters.

Section 9.3

The structures inside a yeast cell have very specific functions.
Metabolism of glucose drives the production of energy in the yeast cell.
The production of off-flavors is due to the overproduction or leaking of compounds from the yeast cell.

Questions to Consider

1. Consider an ideal Carnot heat engine that undergoes the cycle of process as indicted in Fig. 9.14. Let us assume that the working gas is $n = 2$ mol of a mono-atomic ideal gas and that the two temperatures are $T_H = 1200$ K and $T_C = 200$ K. If the volume at point 3 is $V = 0.1$ m^3,

   a. What is the pressure at point 3?
   b. What is the pressure and volume at point 4?
   c. What is the pressure and volume at point 1?
   d. What is the pressure and volume at point 2?
   e. Find the work done for all four processes.
   f. Find the heat energy absorbed and released, Q_H and Q_C.

2. Consider a closed-loop vapor refrigeration system that uses R-134a. The pressure in the condenser is 900 kPa, and the pressure in the evaporator is 100 kPa. If the work input into the system is 600 kW, what is the mass flow rate around the loop? What is the actual COP for this refrigerator? What is the ideal COP?
3. Provide a list of pros and cons for the double-drop system of fermentation.
4. What benefit does the yeast cell obtain from the production of ethanol?
5. Why do yeast go "dormant"? Under what conditions does this occur?
6. What problems would exist with a yeast cell that was deficient in the production of valine? How might a brewer overcome this issue?
7. Consider that you have 1.0 mol of an ideal gas with a pressure of 760 mmHg and temperature of 150 °F. What is the volume of this gas?
8. If the gas in question 7 was heated to 100 °C, what would be the new volume? Assume that the pressure remains constant.
9. How many liters does 1.0 mol of an ideal gas occupy at standard temperature and pressure (273 K and 1 bar)?
10. What likely happens to any fructose that is consumed by a yeast cell?
11. Why are acetate esters the most common of the esters produced by yeast?
12. Which steps in the metabolism of glucose produce carbon dioxide? Which is the main reason that beer is carbonated naturally?
13. What would happen to a sample of fermenting wort if a large quantity of sucrose was added?
14. A brewer accidentally aerates a fermenting wort when they transfer it to a secondary fermenter. Describe what would happen?
15. What is the ultimate fate of the aldehydic carbon in glucose (the anomeric center)? Describe how this happens.
16. What is the benefit of transferring heat while the substance is a mixture of vapor and liquid?
17. Can a system have a COP of 0.80? Explain your answer.
18. Explain the first and second law of thermodynamics.
19. What is the change in the heat energy in an adiabatic process?
20. In your own words, describe how a Venturi aerator works.
21. What is the rate of heat transfer when a 100 °C wort sample is separated from 20 °C water by a 0.2-mm sheet of stainless steel? by a 0.2-mm sheet of aluminum? Which is better at transferring heat?
22. Why does the rate of heat transfer slow down as the hot liquid cools?
23. What is the change in the internal energy if a system does 400 J of work and receives 200 J of heat?
24. What is the efficiency of the system in question 23? If the temperature of the cold fluid was 20 °C, what would be the temperature of the hot fluid?
25. Describe the differences between mannan and starch.
26. If splashing wort into an open fermenter results in about 8–10 ppm oxygen, why would anyone want to use a Venturi aerator?
27. What is the change in work to a system if the pressure stays constant at 1 bar while the volume of the system changes from 1.0 to 1.5 L?

28. What is the definition of a state variable? Is altitude a state variable? Is distance a state variable?
29. In Fig. 9.30, what are the chemical formula for pyruvate and acetaldehyde? Assuming that CO_2 is a product of the transformation, what other atom is missing from the transformation? What is the likely source of this extra atom in the reaction?
30. Use the information in this chapter to sketch what a yeast cell with its internal structures would look like.

Laboratory Exercises

The Effect of Sugars on Fermentation

This experiment is designed to illustrate the differences in fermentation rates using different sugars. The rates can be easily measured by collecting the by-product (carbon dioxide).

Equipment Needed:

Erlenmeyer flasks, 125 mL
Single-holed stoppers to fit flasks
Packet of dry yeast, or uniformly mixed liquid yeast
Stir bars (one per flask) and stirring plates
Glass tube and hose (one set per flask)
Graduated cylinder or gas collection tube (one per flask)
Large dish to use as cold-water bath
Sugars from the following list: (at least three should be used)

Sucrose	Arabinose	Glucose
Glucose	Invert sugar	Fructose
Fructose	Maltotriose	Lactose
Maltose	Starch	Glucitol

Experiment:

Each group should obtain one setup per member of the group. Add 50 mL to each of the Erlenmeyer flasks using a graduated cylinder. Then, measure out 5 grams of each of the monosaccharides and 2.5 g of each of the disaccharides. Dissolve each sugar in the water in its own Erlenmeyer flask. Add a stir bar and 0.5 g of yeast to each flask. Push the glass tube into the stopper, and attach the hose to the end (CAREFULLY to avoid breaking the glass). Insert the stopper in the flask and the end of the hose into a graduated tube filled with water.
The best way to fill the graduated cylinder with water is to lay it flat in a dish of water and then insert the tube. While keeping the open end under the surface of the water, raise the bottom of the graduated cylinder until it is vertical. Then, use a

clamp and ring stand to hold it in place. The cylinder should be free of any bubbles and only filled with water.

Turn on the stir plate to vigorously mix the yeast in the sugar water, and then measure the time it takes each flask to generate 5 mL of gas. This can also be done by recording the time for every 5 mL of gas that is produced and then creating a plot of the time (x-axis) versus the volume (y-axis).

Comment on the production of gas based on the specific sugar. An alternative to this process is to perform the fermentations at different temperatures or with different yeast cultivars.