Liquefaction of Gases

If the temperature and pressure of a gas can be brought into the region between the saturated liquid and saturated vapour lines then the gas will become 'wet' and this 'wetness' will condense giving a liquid. Most gases existing in the atmosphere are extremely superheated, but are at pressures well below their critical pressures. Critical point data for common gases and some hydrocarbons are given in Table 8.1.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Critical temperature $T_c$ [°C]</th>
<th>Critical pressure, $p_c$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (H$_2$O)</td>
<td>374 [647]</td>
<td>221.2</td>
</tr>
<tr>
<td>Methane (CH$_4$)</td>
<td>−82 [191]</td>
<td>46.4</td>
</tr>
<tr>
<td>Ethane (C$_2$H$_6$)</td>
<td>32 [305]</td>
<td>49.4</td>
</tr>
<tr>
<td>Propane (C$_3$H$_8$)</td>
<td>96 [369]</td>
<td>43.6</td>
</tr>
<tr>
<td>Butane (C$<em>4$H$</em>{10}$)</td>
<td>153 [426]</td>
<td>36.5</td>
</tr>
<tr>
<td>Carbon dioxide (CO$_2$)</td>
<td>31 [304]</td>
<td>89</td>
</tr>
<tr>
<td>Oxygen (O$_2$)</td>
<td>−130 [143]</td>
<td>51</td>
</tr>
<tr>
<td>Hydrogen (H$_2$)</td>
<td>−243 [30]</td>
<td>13</td>
</tr>
<tr>
<td>Nitrogen (N$_2$)</td>
<td>−147 [126]</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure 8.1 depicts qualitatively the state point of oxygen at ambient conditions and shows that it is a superheated gas at this pressure and temperature, existing at well above the critical temperature but below the critical pressure. If it is desired to liquefy the gas it is necessary to take its state point into the saturated liquid–saturated vapour region. This can be achieved in a number of ways. First, experience indicates that 'heat' has to be taken out of the gas. This can be done by two means:

(i) cooling the gas by heat transfer to a cold reservoir, i.e. refrigeration;
(ii) expanding the gas in a reversible manner, so that it does work.

8.1 Liquefaction by cooling – method (i)

This method is satisfactory if the liquefaction process does not require very low temperatures. A number of common gases can be obtained in liquid form by cooling.
Examples of these are the hydrocarbons butane and propane, which can both exist as liquids at room temperature if they are contained at elevated pressures. Mixtures of hydrocarbons can also be obtained as liquids and these include liquefied petroleum gas (LPG) and liquefied natural gas (LNG).

A simple refrigerator and the refrigeration cycle are shown in Figs 8.2(a) and (b) respectively.

Consider the throttling process in Fig 8.2, which is between 4 and 1. The working fluid enters the throttle at a high pressure in a liquid state, and leaves it at a lower pressure and temperature as a wet vapour. If the mass of working fluid entering the throttle is 1 kg then the mass of liquid leaving the throttle is \((1 - x)\) kg. If this liquid were then withdrawn to a vessel, and the mass of fluid in the system were made up by adding \((1 - x)\) kg of gas at
Liquefaction by cooling – method (i) 137

state 3 then it would be possible to liquefy that gas. The liquefaction has effectively taken place because, in passing through the throttle, the quality (dryness fraction) of the fluid has been increased, and the energy to form the vapour phase has been obtained from the latent heat of the liquid thus formed: the throttling process is an isenthalpic one, and hence energy has been conserved. If the working fluid for this cycle was a gas, which it was desired to liquefy, then the liquid could be withdrawn at state 1'.

The simple refrigeration system shown in Fig 8.2 might be used to liquefy substances which boil at close to the ambient temperature, but it is more common to have to use refrigeration plants in series, referred to as a cascade, to achieve reasonable levels of cooling. The cascade plant is also more cost-effective because it splits the temperature drop between two working fluids. Consider Fig 8.2: the difference between the top and bottom temperatures is related to the difference between the pressures. To achieve a low temperature it is necessary to reduce the evaporator pressure, and this will increase the specific volume of the working fluid and hence the size of the evaporator. The large temperature difference will also decrease the coefficient of performance of the plant. The use of two plants in cascade enables the working fluid in each section to be optimised for the temperature range encountered. Two plants in cascade are shown in Fig 8.3(a), and the $T$–$S$ diagrams are depicted in Fig 8.3(b).

![Fig. 8.3 Cascade refrigeration cycle](image)

In the cascade arrangement the cooling process takes place in two stages: it is referred to as a binary cascade cycle. This arrangement is the refrigeration equivalent of the combined cycle power station. The substance to be liquefied follows cycle 1–2–3–4–1, and the liquid is taken out at state 1'. However, instead of transferring its waste energy, $Q_2$, to the environment it transfers it to another refrigeration cycle which operates at a higher temperature level. The working fluids will be different in each cycle, and that in the high temperature cycle, 5–6–7–8–5, will have a higher boiling point than the substance being...
liquefied. The two cycles can also be used to liquefy both of the working fluids, n.,
case liquid will also be taken out at state 5'.

The overall coefficient of performance of the two plants working in cascade can be
evaluated by considering the heat flow through each section and is given by

\[
\left(1 + \frac{1}{\beta'} \right) = \left(1 + \frac{1}{\beta_{1}'} \right) \left(1 + \frac{1}{\beta_{2}'} \right)
\]  

(8.1)

where \( \beta' \) is the overall coefficient of the combined plant, and \( \beta_{1}' \) and \( \beta_{2}' \) are the
coefficients of performance of the separate parts of the cascade. The coefficient of
performance of the overall plant is less than that of either individual part.

The liquefaction of natural gas is achieved by means of a ternary cascade refrigeration
cycle, and the components are shown in Fig 8.4. In this system a range of hydrocarbons
are used to cool each other. The longer chain hydrocarbons have higher boiling points
than the shorter ones, and hence the alkanes can be used as the working fluids in the
plant.

Fig. 8.4 Plant for liquefaction of natural gas
Another common gas that can be obtained in a non-gaseous form is carbon dioxide (CO₂). This is usually supplied nowadays in a solid form called dry ice, although it was originally provided as a pressurised liquid. Dry ice is obtained by a modification of the refrigeration process, and the plant and relevant T–s diagrams are shown in Figs 8.5(a) and (b) respectively. This is like a ternary cascade system, but in this case the working fluid passes through all the stages of the plant. The carbon dioxide gas enters the plant at state ‘a’, and passes through the final stage, referred to as the snow chamber, because by this stage the gas has been converted to dry ice. Heat is transferred from the carbon dioxide to the final product causing some evaporation: this evaporated product is passed back to the first compressor. The fluid then passes to the first compressor, where it is compressed to state ‘c’. It is then passed into a flash tank where it is cooled by transferring heat with liquid already in there; this again causes some evaporation of the product, which is passed back into the second compressor, along with the working fluid. In the example shown the process has three stages, and the final stage must be at a pressure high enough
to enable the condensation to occur by heat transfer to a fluid at close to atmospheric temperature, depicted by point ‘h’ in Fig 8.5(b); the pressure must also be below the critical pressure for condensation to occur. The liquid that is produced at ‘j’ passes through the series of throttles to obtain the refrigeration effect necessary to liquefy the carbon dioxide. In the final chamber the liquid is expanded below the triple point pressure, and the phase change enters the solid—gas region. Carbon dioxide cannot exist as a liquid at atmospheric pressure, because its triple point pressure is 5.17 bar; hence it can be either a pressurised liquid or a solid. Dry ice is not in equilibrium with its surroundings, and is continually evaporating. It could only be in a stable state if the ambient temperature were dropped to the equivalent of the saturated temperature for the solid state at a pressure of 1 bar.

### 8.2 Liquefaction by expansion – method (ii)

If the gas does work against a device (e.g. a turbine) whilst expanding adiabatically then the internal energy will be reduced and liquefaction may ensue. A cycle which includes such an expansion process is shown in Fig 8.6. The gas, for example oxygen, exists at state 1 when at ambient temperature and pressure: it is in a superheated state, but below the critical pressure. If the gas is then compressed isentropically to a pressure above the critical pressure it will reach state 2. The temperature at state 2 is above the ambient temperature, $T_a$, but heat transfer to the surroundings allows the temperature to be reduced to state point 2a. If the liquefaction plant is a continuously operating plant, then there will be available a supply of extremely cold gas or liquid and this can be used, by a suitable arrangement of heat exchangers, to cool the gas further to state point 3. If the gas is now expanded isentropically through the device from state 3 down to its original pressure it will condense out as a liquid at state 4. Hence, the processes defined in Fig 8.6 can be used to achieve liquefaction of a gas by use of a device taking energy out of the substance by producing work output. It should be noted that if the gas was a supercritical vapour at ambient conditions it would be impossible to obtain it in liquid form at atmospheric pressure.
In the liquefaction process described above, the gas may be expanded from state 3 to state 4 either by a reciprocating machine or against an expansion turbine. Both these machines suffer the problem that the work done in the expansion process is a function of the initial temperature because the temperature drop across the turbine is

\[ \Delta T = T_3 \eta_T \left[ 1 - \left( \frac{p_4}{p_3} \right)^{(\kappa-1)/\kappa} \right] \quad (8.2) \]

It can be seen from eqn (8.2) that as \( T_3 \) becomes very small, the temperature drop achieved by the expansion gets smaller, which means that the pressure ratio to obtain the same temperature drop has to be increased for very low critical temperatures. Another major problem that occurs at very low temperatures is that lubrication becomes extremely difficult. For this reason the turbine is a better alternative than a reciprocating device because it may have air bearings, or gas bearings of the same substance as that being liquefied, thus reducing contamination.

Fortunately another method of liquefaction is available which overcomes many of the problems described above. This is known as the Joule–Thomson effect and it can be evaluated analytically. The Joule–Thomson effect is the result of relationships between the properties of the gas in question.

### 8.3 The Joule–Thomson effect

The Joule–Thomson effect was discovered in the mid-19th century when experiments were being undertaken to define the First Law of Thermodynamics. Joule had shown that the specific heat at constant volume was not a function of volume, and a similar experiment was developed to ascertain the change of enthalpy with pressure. The
experiment consisted of forcing a gas through a porous plug by means of a pressure drop. It was found that, for some gases, at a certain entry temperature there was a temperature drop in the gas after it had passed through the plug. This showed that, for these gases, the enthalpy of the gas was a function of both temperature and pressure. A suitable apparatus for conducting the experiment is shown in Fig 8.7.

![Fig. 8.7 Porous plug device for the Joule–Thomson experiment](image)

If the upstream pressure and temperature are maintained constant, and the downstream pressure is varied, the temperature measured follows a trace of the form shown in Fig 8.8.

![Fig. 8.8 Isenthalpic curve for flow through a porous plug](image)

Line ABC in Fig 8.8 does not show the change of temperature as the gas flows through the porous plug; it is made up of results from a series of experiments and shows the effect of lowering the back pressure on the downstream temperature. It is very difficult to evaluate the variation of temperature along the plug, and this will not be attempted here. However, as the pressure $p_2$ is decreased below $p_1$ the temperature increases until point B is reached; after this the temperature decreases with decreasing pressure, $p_2$. Eventually a point is reached, denoted C on the diagram, where $T_2 = T_1$, and after this $T_2 < T_1$. The maximum temperature on this isenthalpic curve is referred to as the inversion temperature, and point B is called the inversion point.
The process shown in Fig 8.8 may be analysed by applying the steady flow energy equation (SFEE) across control volume, when

\[
\dot{Q} - \dot{W} = \dot{m} \left( h_2 - h_1 + \frac{V_2^2}{2} - \frac{V_1^2}{2} \right)
\]

(8.3)

where

\[\dot{Q} = \text{rate of heat transfer},\]
\[\dot{W} = \text{rate of work transfer},\]
\[\dot{m} = \text{mass flow rate},\]
\[h_1, h_2 = \text{enthalpy upstream and downstream of plug},\]
\[V_1, V_2 = \text{velocity upstream and downstream of plug}.\]

Now \(\dot{Q} = 0, \dot{W} = 0, V_2 \approx V_1\). Hence \(h_2 = h_1\), and the enthalpy along line ABC is constant; thus ABC is an isenthalpic line. The most efficient situation from the viewpoint of obtaining cooling is achieved if \(p_1\) and \(T_1\) are at B, the inversion point. If state \((p_1, T_1)\) is to the right of B then \(T_2\) depends on the pressure drop, and it could be greater than, equal to or less than \(T_1\). If the upstream state \((p_1, T_1)\) is at B then the downstream temperature, \(T_2\), will always be less than \(T_1\). It is possible to analyse whether heating or cooling will occur by evaluating the sign of the derivative \((\partial T/\partial p)_{s}\). This term is called the Joule-Thomson coefficient, \(\mu\).

If \(\mu < 0\), then there can be either heating or cooling, depending on whether the downstream pressure is between A and C, or to the left of C. If \(\mu > 0\), then the gas will be cooled on passing through the plug (i.e. the upstream state point defined by \((p_1, T_1)\) is to the left of B on the isenthalpic line).

This situation can be analysed in the following way. From the Second Law of Thermodynamics

\[dh = T \, ds + \nu \, dp\]

(8.4)

But, for this process \(dh = 0\), and thus

\[0 = T \left( \frac{\partial s}{\partial p} \right)_h + \nu\]

(8.5)

If it is assumed that entropy is a continuous function of pressure and temperature, i.e. \(s = s(p, T)\), then

\[ds = \left( \frac{\partial s}{\partial p} \right)_T dp + \left( \frac{\partial s}{\partial T} \right)_p dT\]

(8.6)

which can be rearranged to give

\[\left( \frac{\partial s}{\partial p} \right)_h = \left( \frac{\partial s}{\partial p} \right)_T + \left( \frac{\partial s}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_h\]

(8.7)

Hence, substituting this expression into eqn (8.5) gives

\[0 = T \left[ \left( \frac{\partial s}{\partial p} \right)_T + \left( \frac{\partial s}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_h \right] + \nu\]

(8.8)
Now, from the thermodynamic relationships (eqn (6.24)),

\[ T \left( \frac{\partial s}{\partial T} \right)_p = c_p \]

and, from the Maxwell relationships (eqn (6.19d)),

\[ \left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p. \]

Thus

\[ 0 = -T \left( \frac{\partial v}{\partial T} \right)_p + c_p \left( \frac{\partial T}{\partial p} \right)_h + \nu \]

which may be rearranged to give

\[ \left( \frac{\partial T}{\partial p} \right)_h = \frac{1}{c_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_p - \nu \right] = \mu \]  

This can be written in terms of the coefficient of expansion

\[ \beta = \frac{1}{\nu} \left( \frac{\partial v}{\partial T} \right)_p \]

and eqn (8.10) becomes

\[ \mu = \frac{\nu}{c_p} [\beta T - 1] \]

At the inversion temperature,

\[ \left( \frac{\partial T}{\partial p} \right)_h = 0 \quad \Rightarrow \quad T_i = \frac{1}{\beta} \]

It is possible to evaluate the Joule–Thomson coefficient for various gases from their state equations. For example, the Joule–Thomson coefficient for a perfect gas can be evaluated by evaluating \( \mu \) from eqn (8.10) by differentiating the perfect gas equation

\[ p \nu = RT \]

Now

\[ \mu = \frac{1}{c_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_p - \nu \right] \]

and, from eqn (8.13), the derivative

\[ \left( \frac{\partial v}{\partial T} \right)_p = \frac{R}{p} \]

Hence

\[ \mu = \frac{1}{c_p} \left[ T \frac{R}{p} - \nu \right] = 0 \]
This means that it is not possible to cool a perfect gas by the Joule–Thomson effect. This is what would be expected, because the enthalpy of an ideal gas is not a function of pressure. However, it does not mean that gases which obey the ideal gas law at normal atmospheric conditions (e.g. oxygen, nitrogen, etc) cannot be liquefied using the Joule–Thomson effect, because they cease to obey this law close to the saturated vapour line. The possibility of liquefying a gas obeying the van der Waals’ equation is considered below.

Van der Waals’ equation for air may be written, using $a$ and $b$ for air as 1.358 bar (m$^3$/kmol)$^2$ and 0.0364 m$^3$/kmol respectively, as

$$p = \frac{0.083143 T}{(v - 0.0364)} - \frac{1.358}{v^2} \quad (8.15)$$

To assess whether a van der Waals’ gas can be liquefied using the Joule–Thomson effect it is necessary to evaluate the Joule–Thomson coefficient, $\mu$. This is related to $(\partial v/\partial T)_{p}$, which can be evaluated in the following way.

From eqn (8.15), in general form

$$T = \left( p + \frac{a}{v^2} \right) \frac{(v - b)}{\mathcal{R}} \quad (8.16)$$

and hence,

$$\left( \frac{\partial T}{\partial v} \right)_{p} = \frac{1}{\mathcal{R}} \left( p + \frac{a}{v^2} \right) - \left( \frac{v - b}{\mathcal{R}} \right) \left( \frac{2a}{v^3} \right)$$

giving

$$\left( \frac{\partial v}{\partial T} \right)_{p} = \frac{\mathcal{R}}{\left( p + \frac{a}{v^2} \right) - (v - b) \left( \frac{2a}{v^3} \right)} \quad (8.17)$$

Thus, from eqn (8.17), the Joule–Thomson coefficient for a van der Waals’ gas is not zero at all points, being given by

$$\mu = \frac{1}{c_p} \left[ \frac{\mathcal{RT}}{\left( p + \frac{a}{v^2} \right) - (v - b) \left( \frac{2a}{v^3} \right)} - v \right] \quad (8.18)$$

### 8.3.1 MAXIMUM AND MINIMUM INVERSION TEMPERATURES

The general form of van der Waals’ equation, eqn (8.15), can be rewritten as

$$T = \left( p + \frac{a}{v^2} \right) \frac{(v - b)}{\mathcal{R}}$$

The inversion temperature is defined as

$$T_i = v \left( \frac{\partial T}{\partial v} \right)_{p} \quad (8.19)$$
which can be evaluated from eqn (8.16) in the following way:

\[
\left( \frac{\partial T}{\partial v} \right)_p = \frac{1}{\mathcal{R}} \left( p + \frac{a}{v^2} \right) - \left( \frac{v-b}{\mathcal{R}} \right) \left( \frac{2a}{v^2} \right) \\
\Rightarrow v \left( \frac{\partial T}{\partial v} \right)_p = \frac{1}{\mathcal{R}} \left[ v \left( p + \frac{a}{v^2} \right) - (v-b) \left( \frac{2a}{v^2} \right) \right]
\]

(8.20)

It is now necessary to solve for \( v \) in terms of \( T_i \) alone, and this can be achieved by multiplying eqn (8.16) by \( v \) and eqn (8.20) by \( (v-b) \). This gives

\[
vT_i = \left( p + \frac{a}{v^2} \right) \frac{v(v-b)}{\mathcal{R}}
\]

(8.21)

and

\[
(v-b)T_i = \frac{v(v-b)}{\mathcal{R}} \left( p + \frac{a}{v^2} \right) - \frac{(v-b)^2}{\mathcal{R}} \frac{2a}{v^2}
\]

(8.22)

Subtracting eqns (8.21) and (8.22) gives

\[
\left( \frac{v-b}{v} \right) = \sqrt{\frac{\mathcal{R}bT_i}{2a}} = x = 1 - \frac{b}{v}
\]

(8.23)

Substituting eqn (8.23) in eqn (8.15) gives

\[
p = \frac{a}{b^2} \left( 1 - \sqrt{\frac{\mathcal{R}bT_i}{2a}} \right) \left( 3\sqrt{\frac{\mathcal{R}bT_i}{2a}} - 1 \right)
\]

(8.24)

The maximum and minimum inversion temperatures are achieved when the pressure, \( p \), is zero. This gives

\[
\hat{T}_i = \frac{2a}{\mathcal{R}b} \quad \text{and} \quad \check{T}_i = \frac{2a}{9\mathcal{R}b} = \frac{\hat{T}_i}{9}
\]

(8.25)

The value of the critical temperature for a van der Waals' gas is

\[
T_c = \frac{8a}{27\mathcal{R}b}
\]

(8.26)

and hence

\[
\frac{\hat{T}_i}{T_c} = \frac{\text{Maximum inversion temperature}}{\text{Critical temperature}} = 6.75 \quad \text{(8.27a, b)}
\]

\[
\frac{\check{T}_i}{T_c} = \frac{\text{Minimum inversion temperature}}{\text{Critical temperature}} = 0.75
\]

These equations will now be applied to air. The values of \( a \) and \( b \) for air are 1.358 bar \((m^3/kmol)^2\) and 0.0364 \(m^3/kmol\) respectively, and van der Waals' equation for air was given as eqn (8.15). Substituting these values into eqn (8.24), which can be solved as a
The Joule-Thomson effect

quadratic equation in \( T_i \), gives the diagram shown in Fig 8.9. This shows that it is not possible to liquefy air if it is above a pressure of about 340 bar.

![Diagram showing higher and lower inversion temperatures for air](image)

**Fig. 8.9** Higher and lower inversion temperatures for air

The maximum pressure for which inversion can occur is when \( dp/dT = 0 \). This can be related to van der Waals' equation in the following way, using the expression for \( x \) introduced in eqn (8.23):

\[
\frac{dp}{dT} = \frac{dp}{dx} \frac{dx}{dT}
\]

and since \( dx/dT \) is a simple single term expression

\[
\frac{dp}{dT} = 0 \quad \text{when} \quad \frac{dp}{dx} = 0
\]

\[
\frac{dp}{dx} = \frac{a}{b^2} \left[ 3(1 - x) - (3x - 1) \right]
\]

Equation (8.28) is zero when \( 3(1 - x) - (3x - 1) = 0 \), i.e. when \( x = 2/3 \).

Hence the maximum pressure at which inversion can occur is

\[
p = \frac{a}{b^2} \left( 1 - \frac{2}{3} \right) \left( 3 \times \frac{2}{3} - 1 \right) = \frac{a}{3b^2} = 9p_c
\]

Thus the maximum pressure at which a Van der Waals' gas can be liquefied using the Joule-Thomson effect is nine times the critical pressure. Substituting for \( a \) and \( b \) in eqn (8.29) gives the maximum pressure as 341.6 bar.

Figure 8.9 indicates that it is not possible to cool air using the Joule-Thomson effect if it is at a temperature of greater than 900 K, or less than about 100 K. Similar calculations for hydrogen give 224 K and 24.9 K, respectively, for the maximum and minimum inversion temperatures. The maximum pressure at which inversion can be achieved for hydrogen is 117 bar.
The inversion curve goes through the lines of constant enthalpy at the point \( (\partial T/\partial p)_h = 0 \). To the left of the inversion curve, cooling always occurs; to the right, heating or cooling occurs depending on the values of the pressure.

Figure 8.9 may be drawn in a more general manner by replotting it in terms of the reduced pressure \( (p_R) \) and temperature \( (T_R) \) used in the law of corresponding states. This generalised diagram is shown in Fig 8.10. Also shown on that diagram is the saturation line for water plotted in non-dimensional form. For a gas to be cooled using the Joule–Thomson effect it is necessary that its state lies in the region shown in Fig 8.10. Consideration of Table 8.1 shows that for oxygen and nitrogen at atmospheric temperature the values of reduced temperature are 2.10 and 2.38 respectively. Hence, these gases can both be liquefied at pressures up to \( 8p_c \), i.e. approximately 400 and 270 bar respectively. However, hydrogen at atmospheric temperature has a \( T_R \) value of 10, and lies outside the range of the Joule–Thomson effect. To be able to liquefy hydrogen by this method it is necessary to precool it by using another fluid, e.g. liquid nitrogen when the value of \( T_R \) could become as low as 4.2, which is well within the range of inversion temperatures.

**Fig. 8.10 Inversion region in terms of reduced pressure \( (p_R = p/p_c) \) and reduced temperature \( (T_R = T/T_c) \). Note the saturation line.**

### 8.4 Linde liquefaction plant

Many gases are liquefied using the Joule–Thomson effect. This approach is embodied in the Linde liquefaction process, and a schematic of the equipment is shown in Fig 8.11(a), while the thermodynamic processes are depicted in Fig 8.11(b). The Linde process is similar to a refrigerator operating on a vapour compression cycle (i.e. the typical refrigeration cycle), except that it includes a heat exchanger to transfer energy equal to \( Q_A \) and \( Q_B \) from the high temperature working fluid to that which has already been cooled through throttling processes. The two throttling processes depicted in Fig 8.11(a) both bring about cooling through the Joule–Thomson effect. The operating processes in the Linde plant will now be described; it will be assumed that the plant is already operating in steady state and that a supply of liquefied gas exists. The gas is supplied to a compressor at state 1 and make-up gas is supplied at state 11, which is the same as state 1. This is then
compressed to a high, supercritical pressure (which might be hundreds of atmospheres) by a multi-stage reciprocating compressor with inter-stage cooling. The gas finally reaches state 2, and it is then passed through a heat exchanger which cools it to state 3. At this point it is throttled for the first time, and is cooled by the Joule–Thomson effect to state 4 and passed into a receiver. Some of the gas entering the receiver is passed back to the
Liquefaction of gases

compressor via the heat exchanger, and the remainder is passed through a second throttle until it achieves state 6. At this stage it is in the liquid–vapour region of the state diagram, and liquid gas can be removed at state 9. The yield of liquid gas is \( y \), defined by the quality of state point 6 on the \( T\)-\( s \) diagram.

### 8.5 Inversion point on \( p\)-\( v\)-\( T \) surface for water

The Joule–Thomson effect for water was met early in the study of thermodynamics. It was shown that the quality (dryness fraction) of water vapour could be increased by passing the wet vapour through a throttle. This process is an isenthalpic one in which the pressure decreases. The liquid–vapour boundary for water is shown in Fig 8.12, and it can be seen that the enthalpy of the vapour peaks at a value of about 2800 \( \text{kJ/kg} \). If water vapour at 20 bar, with an enthalpy of 2700 \( \text{kJ/kg} \), is expanded through a throttle then its quality increases; this means that it would not be possible to liquefy the water vapour by the Joule–Thomson effect, and hence this point must be below the minimum inversion temperature. Using the van der Waals' relationship and substituting for the critical temperature gives \( T_1 = 0.75 \times T_c = 212^\circ \text{C} \). This is equivalent to a pressure of about 20 bar, which is close to that defining the maximum enthalpy on the saturation line. This point of minimum inversion temperature can also be seen on the Mollier (\( h\)-\( s \)) diagram for steam, and is where the saturation curve peaks in enthalpy value. If the pressure were, say, 300 bar and the enthalpy were 2700 \( \text{kJ/kg} \) then an isenthalpic expansion would result in the gas becoming wetter, and liquefaction could occur.

![Fig. 8.12 Variation of enthalpy on the saturated liquid and vapour lines with pressure for steam](image)

**Example**

A simple Linde liquefaction plant is shown in Fig 8.13. This is similar to that in Fig 8.11 except that the liquefaction takes place in a single process, and the cascade is omitted. The plant is used to liquefy air, which is fed to the compressor at 1 bar and \( 17^\circ \text{C} \), and compressed isothermally to 200 bar. The compressed air then transfers heat in a counterflow heat exchanger, which has no external heat losses or friction, with the stream leaving the flash chamber, and the inlet temperature of the hot stream equals the outlet
temperature of the cold stream. Using the table of properties for air at low temperatures and high pressures (Table 8.2), and taking the dead state conditions for exergy as 1 bar and 290 K, evaluate the:

(i) yield of liquid air per kg of compressed fluid;
(ii) temperature of the compressed air before the Joule–Thomson expansion process;
(iii) minimum work required per kg of liquid air;
(iv) actual work required per kg of liquid air;
(v) rational efficiency of the plant, and the irreversibilities introduced by the heat exchanger and the throttle. (example based on Haywood (1980)).

Fig. 8.13 Simplified Linde gas liquefaction plant: (a) schematic diagram of simplified plant; (b) $T$–$s$ diagram for liquefaction process
Table 8.2 Properties of air (from Haywood, 1972)

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Temperature $T_s$ (K)</th>
<th>Enthalpy ($h$) (kJ/kmol)</th>
<th>Entropy ($s$) (kJ/kmol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$h_f$</td>
<td>$h_g$</td>
</tr>
<tr>
<td>1</td>
<td>81.7</td>
<td>0</td>
<td>5942</td>
</tr>
<tr>
<td>5</td>
<td>98.5</td>
<td>917</td>
<td>6249</td>
</tr>
<tr>
<td>10</td>
<td>108.1</td>
<td>1537</td>
<td>6284</td>
</tr>
<tr>
<td>20</td>
<td>119.8</td>
<td>2506</td>
<td>6127</td>
</tr>
<tr>
<td>30</td>
<td>127.8</td>
<td>3381</td>
<td>5760</td>
</tr>
<tr>
<td>35</td>
<td>131.1</td>
<td>3884</td>
<td>5433</td>
</tr>
<tr>
<td>37.66</td>
<td></td>
<td>4758</td>
<td>4758</td>
</tr>
</tbody>
</table>

**Properties of air on the saturated liquid and saturated vapour lines**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (atmospheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>$h$</td>
</tr>
<tr>
<td></td>
<td>$s$</td>
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<tr>
<td>100</td>
<td>$h$</td>
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<tr>
<td></td>
<td>$s$</td>
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<tr>
<td>110</td>
<td>$h$</td>
</tr>
<tr>
<td></td>
<td>$s$</td>
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<td>120</td>
<td>$h$</td>
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<td></td>
<td>$s$</td>
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<td>125</td>
<td>$h$</td>
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<td></td>
<td>$s$</td>
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<td>$s$</td>
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<tr>
<td>145</td>
<td>$h$</td>
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<td></td>
<td>$s$</td>
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<tr>
<td>150</td>
<td>$h$</td>
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<td>$s$</td>
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<td>160</td>
<td>$h$</td>
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<tr>
<td>170</td>
<td>$h$</td>
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<td>$s$</td>
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<td>$s$</td>
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<td>190</td>
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<td>250</td>
<td>$h$</td>
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<td></td>
<td>$s$</td>
</tr>
<tr>
<td>290</td>
<td>$h$</td>
</tr>
<tr>
<td></td>
<td>$s$</td>
</tr>
<tr>
<td>300</td>
<td>$h$</td>
</tr>
<tr>
<td></td>
<td>$s$</td>
</tr>
</tbody>
</table>

Properties of superheated air at low temperatures and high pressures

$h$: kJ/kmol

$s$: kJ/kmol K

$m_e = 28.9$
Solution

(i) **Yield of liquid per kg of compressed fluid.**

At point 1, \( p_1 = 1 \text{ bar}; \ T_1 = 290 \text{ K}; \ h_1 = 12097 \text{ kJ/kmol} \)

\[ s_1 = 111.63 \text{ kJ/kmol K} \]

at point 2, \( p_2 = 200 \text{ bar}; \ T_2 = 290 \text{ K}; \ h_2 = 11025 \text{ kJ/kmol} \)

\[ s_1 = 64.09 \text{ kJ/kmol K} \]

Considering the heat exchanger: since it is adiabatic

\[ H_2 - H_3 = H_7 - H_6 \]  

(8.30)

Substituting for specific enthalpies in eqn (8.30) gives

\[ m_2(h_2 - h_3) = m_6(h_7 - h_6) \]  

(8.31)

Now

\[ m_6 = m_2(1 - y) \]  

(8.32)

and hence

\[ h_2 - h_3 = (1 - y)(h_7 - h_6) \]

\[ \Rightarrow h_3 = h_2 - (1 - y)(h_7 - h_6) \]  

(8.33)

The process from 3 to 4 is isenthalpic, and is a Joule--Thomson process, thus

\[ h_4 = h_3 \]  

(8.34)

But

\[ h_4 = x_4 h_8 + (1 - x_4) h_f = (1 - y) h_6 + y h_5 \]  

(8.35)

Combining eqns (8.33) and (8.34) gives

\[ y = \frac{h_2 - h_7}{h_7 - h_5} = \frac{12097 - 11025}{12097 - 0} = 0.08862 \]  

(8.36)

Hence, the yield of liquid air per kg of compressed air is 0.08862 kg.

(ii) **The temperature before the Joule--Thomson process.**

This is the temperature of the gas at point 3. From eqns (8.34) and (8.35)

\[ h_3 = h_4 = x_4 h_8 + (1 - x_4) h_f = (1 - y) h_6 + y h_5 \]

\[ = (1 - 0.08862) \times 5942 = 5415 \text{ kJ/kmol} \]  

(8.37)

This value of enthalpy at 200 bar is equivalent to a temperature of 170 K.

(iii) **Minimum work required per kg liquid yield.**

Consideration of the control system in Fig 8.13 shows that only three parameters cross the system boundary; these are the make-up gas, the liquid yield, and the work input to the compressor. Hence, the minimum work
required to achieve liquefaction of the gas is

\[ \dot{W}_{\text{net}} = y(b_1 - b_2), \]

giving the work per unit mass of liquid as

\[ \dot{\omega}_{\text{net}} = \frac{\dot{W}_{\text{net}}}{y} = b_1 - b_5 \]  

(8.38)

In this case, \( b_5 = 0 \) because point 5 (the liquid point at 1 bar) was chosen as the datum for properties; hence

\[ \dot{\omega}_{\text{net}} = h_1 - T_0 s_1 - 0 = 12097 - 290 \times 111.63 = -20275 \text{ kJ/kmol liquid} \]

(iv) **Work required per liquid yield.**

The compression process is an isothermal one, and hence the work done is

\[ w = p_1 v_1 \ln \frac{v_2}{v_1} = -p_1 v_1 \ln \frac{p_2}{p_1} = -RT_1 \ln \frac{p_2}{p_1} \]  

(8.39)

Substituting the values gives

\[ w = -8.3143 \times 290 \times \ln \frac{200}{1} = -12775 \text{ kJ/kmol gas} \]

\[ = \frac{-12775}{28.9} = -442 \text{ kJ/kg gas} = \frac{-442}{0.08863} = -4987 \text{ kJ/kg liquid} \]

(v) **Rational efficiency.**

The rational efficiency of the plant is defined as

\[ \eta_r = \frac{\dot{\omega}_{\text{net}}}{w} = \frac{-701}{-4987} = 0.1406 \]  

(8.40)

Hence, the plant is only 14.1% as efficient as it could be if all the energy transfers were reversible. It is instructive to examine where the irreversibilities occur.

*The heat exchanger*

The irreversibility of the heat exchanger is

\[ I_{\text{HE}} = (1 - y)(b_1 - b_6) - (b_2 - b_3) \]

\[ = 0.91137 \times \{ (-20\ 275 - (-15\ 518)) - \{ -7561 - (-5776) \} \} \]

\[ = -2550 \text{ kJ/kmol gas} \]

This is equivalent to 20.0% of the work required to compress the gas.

*The throttle to achieve liquefaction*

The irreversibility of the throttle is

\[ I_{\text{throttle}} = b_4 - b_3 = 0.91137 \times (-15\ 518) - (-5776) = -8366 \text{ kJ/kmol gas} \]

This is equivalent to 65.5% of the work used to compress the gas.

Hence, the work required to liquefy the gas is

\[ w = \dot{\omega}_{\text{net}} + I_{\text{HE}} + I_{\text{throttle}} \]
8.6 Concluding remarks

It has been shown that gases can be liquefied in a number of ways. Gases which are liquids at temperatures close to ambient can be liquefied by cooling in a simple refrigeration system. Carbon dioxide, which cannot be maintained as a liquid at ambient pressure, is made into dry ice which is not in equilibrium at room temperature and pressure.

If it is necessary to achieve extremely low temperatures to bring about liquefaction, the Joule–Thomson effect is employed. It is possible to analyse such liquefaction plant using equilibrium thermodynamics and suitable equations of state. The efficiency of liquefaction plant has been calculated and the major influences of irreversibilities in the processes have been illustrated.

PROBLEMS

1. Show that the Joule–Thomson coefficient, \( \mu \), is given by

\[
\mu = \frac{1}{c_p} \left( T \left( \frac{\partial v}{\partial T} \right)_p - v \right)
\]

Hence or otherwise show that the inversion temperature \( (T_i) \) is

\[
T_i = \left( \frac{\partial T}{\partial v} \right)_p v
\]

The equation of state for air may be represented by

\[
p = \frac{\mathcal{R}T}{v_m - 0.0367} - \frac{1.368}{v_m^2}
\]

where \( p = \) pressure (bar), \( T = \) temperature (K), and \( v_m = \) molar volume (m\(^3\)/kmol).

Determine the maximum and minimum inversion temperatures and the maximum inversion pressure for air.

[896 K; 99.6 K; 339 bar]

2. The last stage of a liquefaction process is shown in diagrammatic form in Fig P8.2. Derive the relationship between \( p \) and \( T \) for the maximum yield of liquid at conditions \( p_L, T_L, h_L \) for a gas obeying the state equation

\[
(p + \frac{1.368}{v_m^2}) (v_m - 0.0367) = \mathcal{R}T
\]

where \( p = \) pressure (bar), \( v_m = \) molar volume (m\(^3\)/kmol), and \( T = \) temperature (K).

Calculate the pressure for maximum yield at a temperature of 120 K.

\[
[p = \frac{a}{b^2} \left( 1 - \sqrt[3]{\frac{\mathcal{R}bT}{2a}} \right) \left( 3 \sqrt[3]{\frac{\mathcal{R}bT}{2a}} - 1 \right); 62.8 \text{ bar}]
\]
The equation of state for a certain gas is

\[ v_m = \frac{\mathcal{R}T}{p} + \frac{k}{\mathcal{R}T} \]

where \( k \) is a constant. Show that the variation of temperature with pressure for an isenthalpic process from 1 to 2 is given by

\[ T_1^2 - T_2^2 = -\frac{4k}{c_p\mathcal{R}} (p_1 - p_2) \]

If the initial and final pressures are 50 bar and 2 bar respectively and the initial temperature is 300 K, calculate

(a) the value of the Joule–Thomson coefficient at the initial state, and
(b) the final temperature of the gas, given that

\[ k = -11.0 \text{ kJ m}^3/(\text{kmol})^2 \]
\[ c_p,m = 29.0 \text{ kJ/kgmol K.} \]

\[ [3.041 \times 10^{-7} \text{ m}^3/\text{J}; 298.5 \text{ K}] \]

A gas has the equation of state

\[ \frac{p v_m}{\mathcal{R}T} = 1 + Ap(T^3 - 9.75T_c T^2 + 9T_c^2 T) + Bp^2 T \]

where \( A \) and \( B \) are positive constants and \( T_c \) is the critical temperature. Determine the maximum and minimum inversion temperatures, expressed as a multiple of \( T_c \).

\[ [6T_c; 0.5T_c] \]
5 A gas has the equation of state

\[
\frac{pV_m}{RT} = 1 + Np + Mp^2
\]

where \(N\) and \(M\) are functions of temperature. Show that the equation of the inversion curve is

\[
P = -\frac{dN}{dT} \left/ \frac{dM}{dT} \right.
\]

If the inversion curve is parabolic and of the form

\[
(T - T_0)^2 = 4a(p_0 - p)
\]

where \(T_0\), \(p_0\) and \(a\) are constants, and if the maximum inversion temperature is five times the minimum inversion temperature, show that \(a = T_0^2/9p_0\) and give possible expressions for \(N\) and \(M\).

\[
M = T : N = -p_0T + \frac{(T - T_0)^3}{12a} + c
\]

6 In a simple Linde gas liquefaction plant (see Fig 8.13) air is taken in at the ambient conditions of 1 bar and 300 K. The water-jacketed compressor delivers the air at 200 bar and 300 K and has an isothermal efficiency of 70%. There is zero temperature difference at the warm end of the regenerative heat exchanger (i.e. \(T_2 = T_7\)). Saturated liquid air is delivered at a pressure of 1 bar. Heat leakages into the plant and pressure drops in the heat exchanger and piping can be neglected.

Calculate the yield of liquid air per unit mass of air compressed, the work input per kilogram if air is liquefied, and the rational efficiency of the liquefaction process.

[7.76%; 8.39 MJ/kg; 8.84%]