Text Sections 19.8, 19.9, 19.10

Sample Problems 19.8

Suggested Questions 7

Suggested Problems None

Summary States and processes
Work done by a gas
First Law of Thermodynamics
Adiabatic processes
Isothermal (constant temperature) processes
Isochoric (constant volume) processes
Isobaric (constant pressure) processes
Cyclical processes
Free expansion processes

Specific objectives

• Explain what is meant by a thermodynamic process
• Sketch and use $p -V$ diagrams
• Explain and use the First Law of Thermodynamics
• Explain the differences between adiabatic, isothermal, isochoric, isobaric and free expansion processes
Equilibrium states and processes

An equilibrium state of an isolated system is one reached after a “long” time. It can be specified macroscopically by a small number of thermodynamic parameters. For example, an equilibrium state of an ideal gas system can be described using \( n \) (the number of moles of gas – fixed for the system), \( p \) (the pressure) and \( V \) (the volume). Other thermodynamic parameters such as \( T \) (the temperature) can be derived from \( n, p \) and \( V \).

A process is a sequence of operations which takes the system from one equilibrium state to another. During a process energy can be transferred to or from the system as heat and/or as work.

An equilibrium state of an ideal gas system can be represented by a point on a \( p-V \) diagram. Non-equilibrium states cannot because they do not have well defined values of \( p \) and \( T \). Although the initial and final states of a real process can be shown on a \( p-V \) diagram the intermediate states cannot. If however the process is carried out very slowly in a large number of small steps then the system is never far from equilibrium. The process can be represented approximately on a \( p-V \) diagram as a curve joining the end points.

Work done by an expanding gas

Consider a quantity of gas at pressure \( p \) with volume \( V \) enclosed by insulating walls. The gas supports a horizontal piston with area \( A \) carrying a load (see Fig 19-12). The upward force exerted by the gas on the piston has magnitude \( F = pA \). If the load is reduced by an infinitesimal amount the piston will move upwards and the pressure decreases until the upward force again balances the weight of the piston and the load. If the piston moves distance \( dx \) the volume increases by \( dV = A \, dx \). The work done by the gas is

\[
dW = F \, dx = (pA) \, dx = p \, dV
\]

If the volume is increased from \( V_i \) to \( V_f \) by a sequence of such processes the work done by the gas is

\[
W = \int dW = \int_{V_i}^{V_f} p \, dV
\]

\( W \) is equal to the area between the curve for the process on a \( p-V \) diagram and the \( V- \) axis (see Fig 19-13).
In SI, $p$ is measured in pascals (abbreviated as Pa), $V$ in cubic metres and $W$ in joules.

Note that $W$ depends on the process. In general the values of $W$ for two processes between the same initial and final states are not the same.

The work done by the gas is positive if the gas expands, i.e. if $V_f > V_i$, and negative if the gas contracts, i.e. if $V_f < V_i$.

The piston exerts a force of magnitude on the gas in the downward direction. The work done on the gas during the process is minus the work done by the gas in the same process.

It is possible to define the work done during processes by other types of system, e.g. stretched wires, chemical cells, magnets, piezoelectric crystals, etc, etc. Thermodynamics can be applied equally to these other systems. In this course of lectures gases are used as examples to demonstrate the principles involved.

* * *

The First Law of Thermodynamics

Experiment shows that for all processes between a given initial state and a given final state $Q - W$ has a constant value. $Q$ is the heat transferred to the system and $W$ the work done by the system during the process.

It follows that there is a thermodynamic parameter, the internal energy, associated with all equilibrium states such that for a process between initial and final equilibrium states with internal energies $E_{int,i}$ and $E_{int,f}$ respectively

$$\Delta E_{int} = E_{int,f} - E_{int,i} = Q - W$$

Note that this equation, the First Law of Thermodynamics, defines differences in internal energy but not the values of the internal energies individually.

Note also that $E_{int}$ like $p$, $V$ and $T$ is a quantity associated with an equilibrium state but $Q$ and $W$ are associated with processes. In particular it does not make sense to speak about the amount of work or the heat in an equilibrium state.

The First Law is a statement of energy conservation. Most modern textbooks write it in terms of the work done on the system rather than the work done by the system. The RHS then becomes $Q + W$ and the Law states that the increase in internal energy of the system is equal to the total energy transferred to the system either by heat or by work. The form of the Law in HRW is based on engineering considerations.
Some special types of processes

**Adiabatic** means no heat flow (see Fig 19-14). This usually means that the system is very well insulated from its surroundings. Sometimes it means that the process occurs so rapidly that there is no time for heat to be transferred to the system, e.g. in sound waves in air. In this case \( Q = 0 \) and \( \Delta E_{int} = - W \).

**Isothermal** means at constant temperature. Both \( Q \) and \( W \) are non-zero.

**Isochoric** means at constant volume. In this case \( W = 0 \) and \( \Delta E_{int} = Q \).

**Isobaric** means at constant pressure. In this case both \( Q \) and \( W \) are non-zero and \( W = p ( V_f - V_i ) \).

**Cyclic** means the final state is the initial state. The process is a closed loop on a \( p-V \) diagram. In this case both \( Q \) and \( W \) are non-zero. \( \Delta E_{int} = 0 \) and hence \( Q = W \).

**Free expansion** A gas expands into a vacuum (see Fig 19-15). No heat is transferred to the system (i.e. adiabatic) and no work is done by the system. Hence \( Q = 0 \), \( W = 0 \), and \( \Delta E_{int} = 0 \). Even though there are well-defined initial and final states that can be plotted on a \( p-V \) diagram the process itself cannot be.