2.4 SPECIAL THERMODYNAMIC PROCESSES

The state of a system can change as a result of interaction with the environment. The change in a system can be fast or slow and large or small. The manner in which the state of a system changed from an initial state to a final state is called a **thermodynamic process**. For analytic purposes in thermodynamics it is helpful to divide up processes as either quasi-static or non-quasi-static as explained below.

2.4.1 Quasi-static and Non-quasi-static Processes

A **quasi-static process** refers to an idealized or imagined process where the change in state is made infinitesimally slowly so that at each instant the system can be assumed to be in a thermodynamic equilibrium within itself and with the environment. For instance, imagine heating 1 kg of water from a temperature 20°C to 21°C at a constant pressure of 1 atmosphere. To heat the water very slowly we may imagine placing the container with water in a large bath which can be slowly heated such that the temperature of the bath can rise infinitesimally slowly from 20°C to 21°C. If we put 1 kg water at 20°C directly into a bath which is at 21°C, the temperature of water will rise rapidly to 21°C in a non-quasi-static way.

Quasi-static processes are done slowly enough that the system remains at thermodynamic equilibrium at each instant despite the fact that system changes over time. The thermodynamic equilibrium of the system is necessary for the system to have well-defined values of macroscopic properties such as the temperature and the pressure of the system at each instant of the process. Therefore, quasi-static processes can be shown as well-defined paths in state space of the system.

Since quasi-static processes cannot be completely realized for any finite change of the system, all processes in nature are nonquasistatic. Examples of quasi-static and non-quasi-static processes are shown in Fig. 2.5. Despite the fact that all finite changes must occur essentially non-quasi-statically at some stage of the change, we can imagine performing infinitely many quasi-static process corresponding to every quasi-static process. Since quasi-static process lend can be analyzed analytically, we will mostly study quasi-static processes in this book. We have already seen that in a quasi-static process the work by a gas is given by pdV. Even the heat can be written in analytic form if the

quasi-static process is also reversible as explained in the chapter on Entropy.
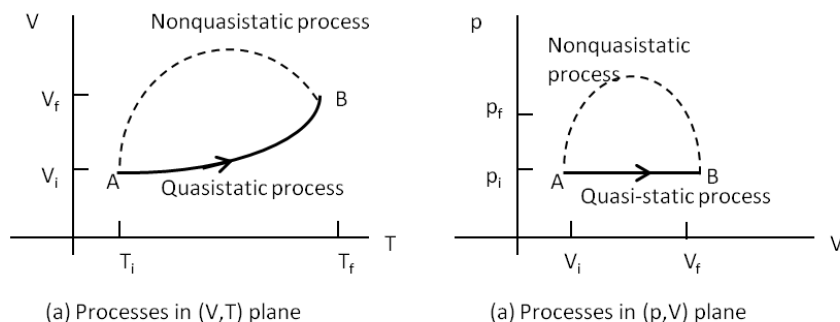

Figure 2.5: Quasi-static and nonquasistatic processes between states A and B of a gas. In a quasi-static process the path of the process between A and B can be drawn in a state diagram since all the states the system goes through are known. In a nonquasistatic process the states between A and B are not known, and hence no path can be drawn. For a gas, you can draw a process in a plane of any pair of two state variables. In (a) the process is drawn in (V, T) plane, and in (b) in the (p, V) plane.

2.4.2   Isothermal Process

An **isothermal process** is a change in the state of the system at a constant temperature. This process is accomplished by keeping the system in thermal equilibrium with a large heat bath during the process. Recall that a heat bath is an idealized "infinitely" large system whose temperature does not change. In practice, the temperature of a finite bath is controlled by either adding or removing a finite amount of energy as the case may be.

As an illustration of an isothermal process, consider a cylinder of gas with a movable piston immersed in a large water tank whose temperature is maintained constant. Since the piston is freely movable, the pressure inside P_{in} is balanced by the pressure outside P_{out} by some weights on the piston (Fig. 2.6).

As weights on the piston are removed, an imbalance of forces on the piston develops. The net non-zero force on the piston would cause the piston to accelerate, resulting in an increase in volume. The expansion of the gas cools the gas to a lower temperature, which makes it possible for the heat to enter from the heat bath into the system until the temperature of the gas is reset to the temperature of the heat bath. If weights are removed in infinitesimal steps, the
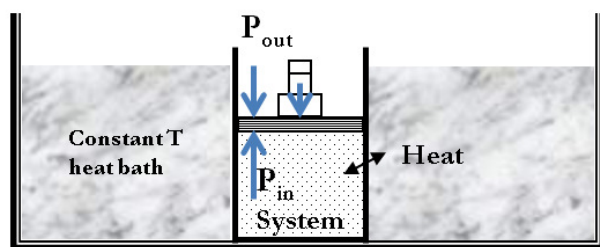
Figure 2.6: Expanding a system at a constant temperature. Removing weights on the piston leads to an imbalance of forces on the piston which causes the piston to move up. As the piston moves up the temperature is lowered momentarily which cause heat to flow from the heat bath to the system. The energy to move the piston eventually comes from the heat bath.

pressure in the system will decrease infinitesimally slowly. This way, an isothermal process can be conducted quasi-statically, which we can represent by a line in (T, p), (T, V) or (p, V) plane of the gas. On (T, p) and (T, V) diagrams a quasi-static isothermal process will be a straight line perpendicular to the temperature axis, while in the (p, V) diagram, an isothermal is usually a curved line as shown in Fig. 2.7. For an ideal gas an isothermal process is hyperbolic since $p \sim \frac{1}{V}$ for an ideal gas at constant temperature.
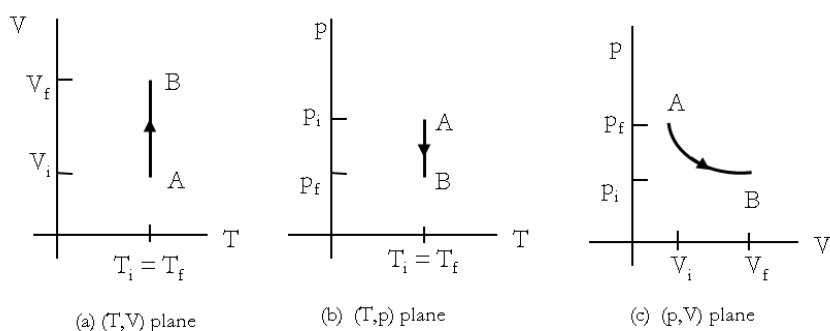

Figure 2.7: An isothermal expansion from a state labeled A to another state labeled B in three planes of (p,V,T) space.

An isothermal process is always conducted quasi-statically, since it to be isothermal throughout the change of volume, you must be able to state the temperature of the system at each step, which is possible only if the system is in thermal equilibrium continuously. Of course, the system must go out of equilibrium for the state to change, but for a quasi-static processes we imagine that the process is conducted in infinitesimal steps such that these departures from

equilibrium can be made as brief and as small as we like.

In the pV plane different temperatures correspond to different curves called **isotherms**. In Fig. 2.8 I have plotted isotherms at various temperatures for an ideal gas by using the ideal gas law, $pV = nRT =$ constant, for an isotherm. Different isotherms correspond to different values of T.
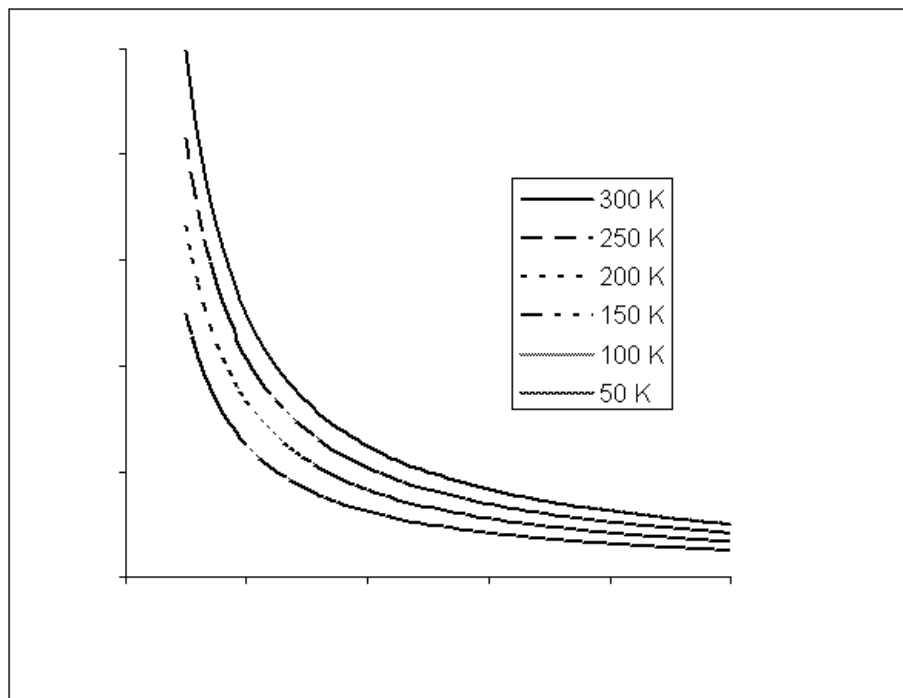

Figure 2.8: Isotherms of one mole of an Ideal Gas. Each isotherm shows the states that can be reached by isothermal process from a point on the curve.

Other quasi-static processes of interest for gases are **isobaric** and **isochoric** processes. An isobaric process is a process where the pressure of the system does not change while an isochoric process is a process where the volume of the system does not change.

2.4.3 Adiabatic Process

In an **adiabatic process**, the system is insulated from its environment so that although the state of the system changes, no heat is allowed to enter or leave the system. An adiabatic process can be conducted either quasi-statically or nonquasistatically. When a system expands adiabatically, it must do work against the outside world, and therefore its energy goes down, which is reflected in lowering of the temperature of the system. An adiabatic expansion leads to lowering of temperature and an adiabatic compression to the increase of temperature.
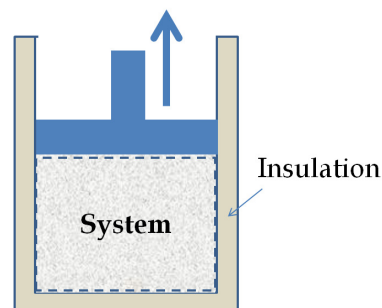

Figure 2.9: Adiabatic expansion. In an adiabatic expansion, there are two time scales: rate of the process and the rate at which heat may enter the system through the walls. If the expansion occurs within a time frame in which negligible heat can enter the system, then the process is called adiabatic. Ideally, during an adiabatic process no heat will enter or exit the system.

2.4.4 Cyclic Process

We say that a system goes through a cyclic process, if the state of the system at the end is same as the state at the beginning. Therefore, state properties such as temperature, pressure, volume, and internal energy of the system do not change over a complete cycle.

$$\Delta U|_{\text{cyclic process}} = 0. \tag{2.19}$$

When the first law of thermodynamics is applied to a cyclic process we obtain a simple relation between heat into the system and the work done by the system over the cycle.

$$Q = W \quad \text{(cyclic process)} \tag{2.20}$$

Example 2.4.1. Path-dependent Work.

A gas in a cylinder undergoes change from an initial state i to a final state f shown in Fig. 2.10 through three paths, i-a-f, i-b-f, and i-f. Find work done by the gas for each path.

Solution. Path i-a-f: This path has two segments: i-a and a-f. On the segment i-a, the volume V does not change, therefore pdV is zero at all elements of the path. On the segment a-f, the pressure is constant, therefore, the integral becomes just a product of the constant pressure and the change in volume. Therefore, on path i-a-f, work done on the system is

$$W_{i\text{-}a\text{-}f} = p_0 \times (4V_0 - V_0) = 3p_0V_0.$$

Path i-b-f: This path also has two segments: i-b and b-f. On the segment i-b, the pressure p is constant with value $3p_0$ and the volume
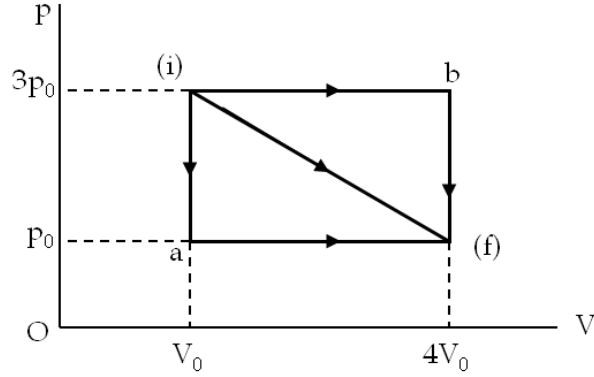
Figure 2.10: Example 2.4.1.

changes from V_0 to $4V_0$. By conducting a similar integral to the one done for the segment a-f, we obtain the following.

$$W_{i\text{-}b} = 3p_0 \times (4V_0 - V_0) = 9p_0V_0.$$

The work done on the segment b-f is zero since the volume is constant for this process. Hence, the work done by the gas on the path i-b-f is

$$W_{i\text{-}b\text{-}f} = 9p_0V_0,$$

which is different than on path i-a-f between the same initial and final states i and f.

Direct path i-f: We can find the work done in two different ways - (i) by using area under the curve and sign according to whether the process is an expansion of compression and (ii) analytically. We will illustrate both method.

(i) Using area-under-the-curve method.

The area under the curve is that of a rectangle and a triangle. Since the process is an expansion, work done will be negative.

$$W_{i\text{-}f} = \left(p_0 \times 3V_0 + \frac{1}{2} \times 2p_0 \times 3V_0\right) = 6p_0V_0.$$

(ii) Analytically by Integrating

On this path both p and V vary, and their mutual variation is related by equation of a straight line.

$$p(V) = 3p_0 - \frac{2p_0}{3V_0}(V - V_0).$$

The work done is now obtained by substituting p in the integrand in

Eq. 2.17 and integrating.

$$
\begin{aligned}
W_{i\text{-}f} &= \int_{V_i}^{V_f} p(V)dV \\
&= \int_{V_0}^{4V_0} \left[3p_0 - \frac{2p_0}{3V_0}(V - V_0) \right] dV \\
&= 3p_0 \times 3V_0 - \frac{2p_0}{3V_0} \left[\frac{1}{2}\left(16V_0^2 - V_0^2\right) - 3V_0^2 \right] \\
&= 6p_0 V_0.
\end{aligned}
$$

The work on the direct path is different from the work on the other paths. Clearly work done on the system here is path-dependent.

Example 2.4.2. Work in Isothermal Process for an Ideal Gas.
Consider a cylinder with a movable piston containing n moles of an ideal gas. The entire apparatus is immersed in a constant temperature bath of temperature T degrees Kelvin. The piston pushes slowly outward on an external body which matches the force momentarily at each instant so that the gas expands quasi-statically from a volume V_1 to V_2 at constant temperature T. Find work done by the gas on the external body.

Solution. Fig. 2.11 shows the isothermal process in the pV plane. At each point the gas obeys the ideal gas law, $pV = nRT$. Since T is constant in an isothermal process, pressure p is the following function of volume.
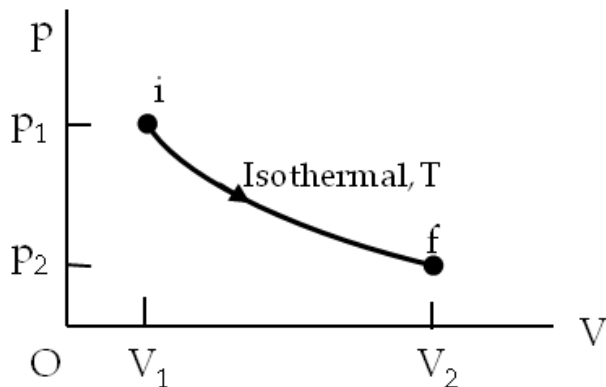

Figure 2.11: Example 2.4.2.

$$
p(V) = (nRT)\frac{1}{V},
$$

where (nRT) is constant. Since the process is quasi-static, work on the gas will be given by the integral over $-pdV$.

$$
W = \int_{V_1}^{V_2} (nRT)\frac{1}{V}dV = nRT\ln\left(\frac{V_2}{V_1}\right).
$$

Since $V_2 > V_1$ for an expansion, the work done by the gas would be positive for an expansion, as expected. In a compression, work is done by the gas will be negative since $V_2 < V_1$. When the gas expands, energy in the gas is transferred to the external body against which the gas is pushing.

Example 2.4.3. Work in an Isothermal Process for a van der Waals gas. Consider a cylinder with n moles of a van der Waals gas with a movable piston. The entire apparatus is immersed in a constant temperature bath of temperature T degrees Kelvin. The piston is then pulled slowly so that the gas expands quasi-statically from a volume V_1 to V_2 at constant temperature T. Find work done by the gas.

Solution. For a van der Waals gas we must use van der Waals equation to express p in terms of V.

$$p(V) = -\frac{a}{V^2} + \frac{nRT}{V - b} \quad \text{(van der Waals gas)}$$

Therefore the work by the gas during the change in the volume from V_1 to V_2 at a constant temperature T is

$$W = \int_{V_1}^{V_2} p(V)dV = a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT \ln \frac{V_2 - b}{V_1 - b}.$$

2.4.5   Infinitesimal First law of thermodynamics

The first law of thermodynamics can be applied to any system in the universe. Suppose a system A interacts with the other systems B such that in an infinitesimal time dt an infinitesimal amount of heat dQ comes into A and A does an infinitesimal amount of work dW, then the first law gives the change in energy dU of A in a differential form as

$$dU_A = dQ_{\text{into A}} - dW_{\text{by A}}. \tag{2.21}$$

This infinitesimal equation is applicable to all closed systems. In a hydrostatic system, such as gas in a tank, work is done as a result of change of volume. Therefore, in these systems we can write the energy involved in the work by the system in another form. This type of system is very useful system for exploring quantitative implications of thermodynamic principles in significant detail. Many of the examples in this book will come from these systems.

   To derive the form of the first law of thermodynamics in hydrostatic systems, consider a tank of gas in equilibrium with the environment. Let the tank have a freely movable piston and the conduct

heat so that initially, say $t = 0$, the pressure p_{in} inside the gas is equal to the pressure outside p_{out}, and temperature T_{in} inside the gas is equal to the temperature T_{out} outside. We can denote the common pressure by p and the common temperature by T.

Suppose we pull the piston outward very slowly so that the volume of the gas increases by amount dV but the pressure in the gas is maintained at p all the time. This type of process, called **quasi-static**, has to be conducted infinitesimally slowly so that the gas is in equilibrium with the environment at all times. The gas will do a work pdV and an infinitesimal amount of heat dQ will enter the gas during this process. Therefore the change in internal energy of the gas for an infinitesimal process in this system will be given by the following relation.

$$\boxed{dU = dQ - pdV \quad \text{(dQ¿0 for Q into gas.)}} \tag{2.22}$$

Since a finite quasi-static process can be built out of infinitely many infinitesimal quasi-static processes, the change over a finite quasi-static process can be obtained by summing over the changes over infinitesimal processes. This leads to a sum over dQ of each process and integrals over dU and pdV.

In these systems although we are able to replace work by an integral, we are cannot replace heat by an integral unless the process is also so-called reversible. We will learn about reversible processes in the chapter on Entropy. It is interesting to note that in these systems, if a process is conducted at a constant volume, then

$$dU = dQ \quad \text{(Constant volume process.} \tag{2.23}$$

Therefore, if you keep a gas in a rigid container so that the volume cannot change, then heating or cooling the gas will exchange heat exactly equal to the change in the energy of the gas.