

Physics 161: Thermodynamics

Lecture #3

More on Changes in State Functions

Let us begin by describing a third approach to the same problem of heating and compressing a gas from an initial temperature and pressure T_1, P_1 , to a final temperature and pressure T_2, P_2 .

The volume V is a state function which is determined by specification of two variables T , and P . To express this, we write

$$V = V(T, P),$$

to indicate that “ V is a function of T and P ”. Differentiating both sides of the equation, the relation between a small change in V and small changes in T and P can be written as follows by using the chain rule:

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP. \quad (1)$$

The subscript P on the derivative $\left(\frac{\partial V}{\partial T} \right)_P$ is to indicate that the derivative of V is to be taken with respect to T holding P constant. The use of the symbol ∂ rather than d in the differentiation serves as redundant reminder of the same thing - that the derivative is to be taken with respect to one variable while holding another variable constant. This is referred to as a *partial* derivative.

The partial derivatives $\left(\frac{\partial V}{\partial T} \right)_P$ and $\left(\frac{\partial V}{\partial P} \right)_T$ are quantities that are determined from experimentation. In 1662 Robert Boyle established a relation for the compressibility of gases at *constant temperature*. He found that the volume varies inversely with the pressure;

$$V = \frac{k_1}{P},$$

where k_1 is a constant. Taking the derivative of Boyle’s law with respect to P , we see that Boyle’s measurement indicates that

$$\left(\frac{\partial V}{\partial P} \right)_T = \frac{-k_1}{P^2} = -\frac{V}{P}. \quad (2)$$

In 1780 Jacques Charles investigated the thermal expansion of gases at *constant pressure*. He found from experiment that

$$V = k_2 T,$$

where k_2 is another constant. This implies that

$$\left(\frac{\partial V}{\partial T} \right)_P = k_2 = \frac{V}{T}. \quad (3)$$

Substituting (2) and (3) into (1), we have the relation

$$dV = \frac{V}{T}dT - \frac{V}{P}dP.$$

Dividing both sides of the equation by V gives

$$\frac{dV}{V} = \frac{dT}{T} - \frac{dP}{P}.$$

At this point we can formally integrate the equation:

$$\begin{aligned}\int_1^2 \frac{dV}{V} &= \int_1^2 \frac{dT}{T} - \int_1^2 \frac{dP}{P} \\ \ln V|_1^2 &= \ln T|_1^2 - \ln P|_1^2; \\ \ln \frac{V_2}{V_1} &= \ln \frac{T_2}{T_1} - \ln \frac{P_2}{P_1}.\end{aligned}$$

Exponentiating both sides, we have

$$\begin{aligned}e^{\ln \frac{V_2}{V_1}} &= \frac{V_2}{V_1} \\ &= e^{\ln \frac{T_2}{T_1} - \ln \frac{P_2}{P_1}} = \frac{T_2}{T_1} \frac{P_1}{P_2}.\end{aligned}$$

Rearranging terms, we see that by combining Boyle's and Charles's laws we have obtained the ideal gas equation of state,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{constant}.$$

Once again, we see that the relation between the final volume V_2 and the initial volume V_1 is given by

$$V_2 = V_1 \frac{T_2}{T_1} \frac{P_1}{P_2}$$

It is important to note that the change in volume,

$$\Delta V \equiv V_2 - V_1 = V_1 \left(\frac{T_2}{T_1} \frac{P_1}{P_2} - 1 \right)$$

is independent of the particular manner, i.e. *path*, by which the heating and compression are carried out, and only depends on the difference between properties of the initial state 1 and the final state 2. That this should be the case is obvious because we never mentioned a path, but also directly from the left hand side of equation (1); as you know, the integral of a perfect differential dV always gives the difference

$$\int_1^2 dV = V|_1^2 = V_2 - V_1$$

between the upper and lower limits of integration, regardless of the path which is followed to go from one to the other.

The First Law of Thermodynamics (1840)

“Energy is conserved when heat is taken into account”

We now turn to a discussion of the first law of thermodynamics. Let us introduce the symbol U to stand for the total energy of the system. It is usually referred to as the *internal* energy to stress that U is the energy of the system alone, the sum of the potential and kinetic energies of the constituent particles that make up the system. The first law is often written as follows:

$$\Delta U = Q - W.$$

In keeping with the sign convention used in your textbook, Q is the heat added to the system *from* the surroundings, and W is the work done *by* the system *on* the surroundings. This is a conservation law because it implies that any change in energy of the system must be accounted for by bringing energy in from the surroundings.

Couldn't the law of conservation of energy instead be expressed by a statement asserting that energy is constant, something along the lines of

$$U = \text{constant?}$$

Indeed it could, but it is the energy of the entire universe that is constant, not the small subset of the universe that we call the system. If we want to talk about the energy of the system and surroundings together, we could write

$$U_{\text{universe}} = \text{constant},$$

with a subscript indicating that we are considering more than just the system. By "universe", we mean the system and the surroundings taken together. In such a case, we can say that

$$\Delta U_{\text{universe}} = 0.$$

which is probably more along the lines of what you had expected for a conservation law. Because

$$U_{\text{universe}} = U_{\text{system}} + U_{\text{surroundings}},$$

it follows that

$$\Delta U_{\text{universe}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0.$$

You can see that this is satisfied by writing

$$\Delta U_{\text{system}} = Q - W$$

for the system, and the same expression for the surroundings but with opposite signs on the heat and work,

$$\Delta U_{\text{surroundings}} = -Q + W.$$

In other words, the heat added to the system by the surroundings is the negative of the heat added to the surroundings by the system, and the work done by the system on the surroundings is the negative of the work done by the surroundings on the system. It follows that when you add ΔU_{system} and $\Delta U_{\text{surroundings}}$ together you get zero.

The internal energy clearly depends on the state of the system. Since the state of the system is determined by just two state variables, such as T and V , or T and P , or P and V , it therefore follows that an expression for U can be written down expressing its dependence on any two state variables. We can write $U = U(T, V)$ as a function of T and V , or we can write $U = U(T, P)$ as a function of T and P , or we can write $U = U(P, V)$ as a function of P and V . We will discuss specific examples of these functions for different fluids later. For the time being it is enough to realize that such relations imply that U can also be regarded as a state variable in its own right. As with any state variable, the change in energy,

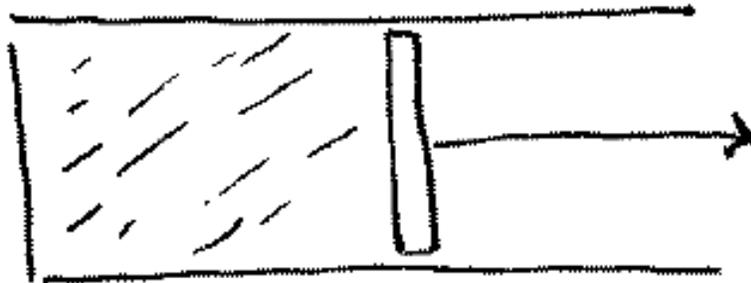
$$\Delta U = U_2 - U_1 = \int_1^2 dU$$

between state 1 and state 2 is independent of path, and only depends on the values of U at initial state 1 and the final state 2.

Let us now discuss a quantity about which we know a great deal: Work. We understand from our studies of mechanics that work is equal to the integral of force over distance;

$$W = \int_{x_1}^{x_2} F dx.$$

In the case of a fluid, we can perform mechanical work by compressing or expanding the fluid with a piston which is fitted into a cylindrical container. For a



piston of area A , the force F is given in terms of the pressure

$$P = F/A$$

on the face of the piston, and thus the work done by the fluid in moving the piston from a point x_1 to a point x_2 is given by

$$\begin{aligned} W &= \int_{x_1}^{x_2} \frac{F}{A} A dx \\ &= \int_{x_1}^{x_2} P A dx \\ &= \int_{V_1}^{V_2} P dV \end{aligned}$$

where in the last line we have recognized that the incremental volume change of the fluid

$$dV = A dx$$

is the product of the piston area A and the differential length dx . So as not to blur the distinction between the system and the surroundings, we will always assume that there is no friction between the walls of the cylinder and the piston.

In equilibrium, the pressure P exerted on the piston by the fluid must be the same as the external pressure P_{external} exerted on the piston by the surroundings. Otherwise the piston would move. If we increase P_{external} , then the piston will move in. If we decrease P_{external} , the piston will move out. Such movements obviously take the fluid out of mechanical equilibrium, and therefore during an expansion or compression we expect that

$$P \neq P_{\text{external}}$$

We don't really know how to quantify P of the fluid while the piston is sliding. Turbulence can be created, so that in some regions of the fluid a pressure gauge would read high, while in other regions the same gauge would read low. Basically, the fluid is taken out of equilibrium while the piston is sliding, so the state variables P , as well as T , become meaningless (it still has a meaningful volume). How then do we calculate work? The answer is that we can use a gadget to monitor P_{external} , and we can use another gadget to keep track of the changes in volume dV , and keep a list of data showing P_{external} and V for the duration of the process. As long as we have this data set, no matter what happens to the fluid within, the work done by the system on the surroundings can be determined by summing up $P_{\text{external}} dV$, that is,

$$W = \int_{V_1}^{V_2} P_{\text{external}} dV.$$

The accuracy with which the work can be calculated depends on the amount of data we collect during the process. Let us consider some examples.

Example 1:

Suppose that 10 moles of ideal gas are confined to a piston at a pressure of $P_1 = 100$ atm and a temperature $T_1 = T$. If the gas is expanded isothermally against a constant external pressure of 1 atm, how much work will be done on the surroundings by the system?

We envision that the gas is initially compressed by an external pressure of 100 atm which is applied to a piston-fitted cylinder. Let us assume that the cylinder has been fitted with a thermometer so that one can monitor the temperature of the gas within. The gas is held at 100 atm until its temperature reaches that of the surroundings. At this point it is in equilibrium, and the initial volume V_1 is recorded. The piston is then to be held in place by removable stops or pins while the external pressure is then lowered to 1 atm. When the pins are suddenly removed, the piston flies out, presumably sloshes back and forth a few times, and eventually comes to rest, all the time while moving against an external pressure of 1 atm. When the thermometer indicates that the temperature of the gas is again T (A process is said to have been carried out *isothermally* when the initial and final temperatures are the same.), the final volume V_2 is recorded. The work is then calculated as

$$\begin{aligned} W &= \int_1^2 P_{\text{external}} dV \\ &= P_{\text{external}} \int_1^2 dV \\ &= P_{\text{external}} (V_2 - V_1) \end{aligned}$$

Notice that we are able to bring P_{external} outside the integration because it is constant. The final and initial volumes are at equilibrium, and hence we can substitute the equation of state for the ideal gas and write

$$W = P_{\text{external}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

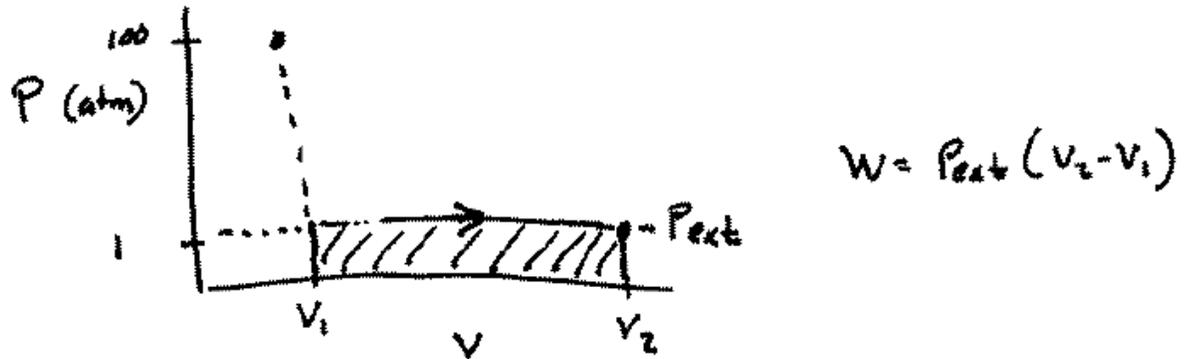
The final pressure P_2 must be equal to the external pressure, and the final temperature is equal to the initial temperature;

$$\begin{aligned} W &= P_{\text{external}} \left(\frac{nRT}{P_{\text{external}}} - \frac{nRT}{P_1} \right) \\ &= nRT \left(\frac{P_{\text{external}}}{P_{\text{external}}} - \frac{P_{\text{external}}}{P_1} \right) \\ &= nRT \left(1 - \frac{1}{100} \right) \\ &= 0.99nRT. \end{aligned}$$

For the isothermal expansion,

$$W_{\text{expansion}} = 9.9RT.$$

The work can be shown as the area under a curve on a $P - V$ diagram:



The two points at the beginning and end of the process are points where the gas is in equilibrium.

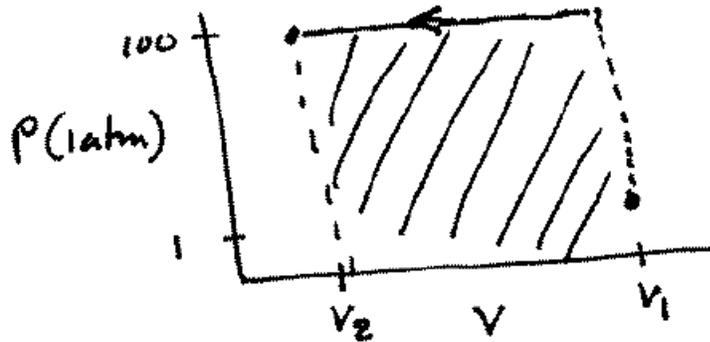
Example 2:

Suppose now that the process is carried out in reverse. Let us insert stops into the piston and return the external pressure to 100 atm. In this case, the initial pressure $P_1 = 1$ atm, and the final pressure $P_2 = 100$ atm. When the stops are removed, the gas is compressed from a volume V_1 (which was the final volume in example 1) to a volume V_2 (which was the initial volume in example 1). For the isothermal compression, we have

$$\begin{aligned}
 W &= P_{\text{external}} \left(\frac{nRT}{P_{\text{external}}} - \frac{nRT}{P_1} \right) \\
 &= nRT \left(\frac{P_{\text{external}}}{P_{\text{external}}} - \frac{P_{\text{external}}}{P_1} \right) \\
 &= nRT \left(1 - \frac{100}{1} \right) \\
 &= -99nRT.
 \end{aligned}$$

$$W_{\text{compression}} = -990RT$$

The work is negative because we have defined W to be the work done on the surroundings by the system, but to compress the gas, it is the surroundings which has to do work on the system. The work is the negative of the area shown on the PV diagram.



$$W = P_{ext} (V_2 - V_1)$$

The combined processes in Example 1 and Example 2 represent what is called a *cyclic* process, in which the gas was returned to the same state with which it started. Thus for the cyclic process, all functions of state return to their original values. Since the energy of the gas is the same as it was at the beginning, we can write

$$\Delta U = 0 \quad (\text{cyclic process})$$

On the other hand, the net work for the cyclic process,

$$\begin{aligned} W_{\text{cycle}} &= W_{\text{expansion}} + W_{\text{compression}} \\ &= (9.9 - 990) RT \\ &= -980.1 RT \end{aligned}$$

is not zero! We had to do 100 times as much work on the gas to recompress it than we were able to extract from the gas when it originally expanded. If the gas is returned to the same energy at the end of the cycle, how does one account for all of this extra work? Apparently it went into heat which was transferred to the surroundings. From the first law, we have

$$\begin{aligned} Q &= \Delta U + W \\ &= 0 - 980.1 RT \\ &= -980.1 RT \end{aligned}$$

The heat transferred to the system from the surroundings is negative, which is an awkward way of saying that heat was transferred to the surroundings from the system. This is a particular illustration of the second law of thermodynamics, which loosely asserts you that you can “never break even”. Once a process has occurred, it is impossible to restore a system to its initial state without dumping heat into the surroundings.

Example 3:

Let us repeat the isothermal expansion of 10 moles of ideal gas which was carried out in Example 1, but this time let us carry it out in two stages. Initially the pressure will be $P_1 = 100$ atm. In stage 1, the external pressure is to be lowered to $P_{\text{external}} = 50$ atm, and held constant. When released, the piston flies outwards, doing work against a constant pressure,

$$\begin{aligned}
 W_1 &= P_{\text{external}} (V_2 - V_1) \\
 &= P_{\text{external}} \left(\frac{nRT}{P_{\text{external}}} - \frac{nRT}{P_1} \right) \\
 &= nRT \left(\frac{P_{\text{external}}}{P_{\text{external}}} - \frac{P_{\text{external}}}{P_1} \right) \\
 &= nRT \left(1 - \frac{50}{100} \right) \\
 &= 0.5 nRT.
 \end{aligned}$$

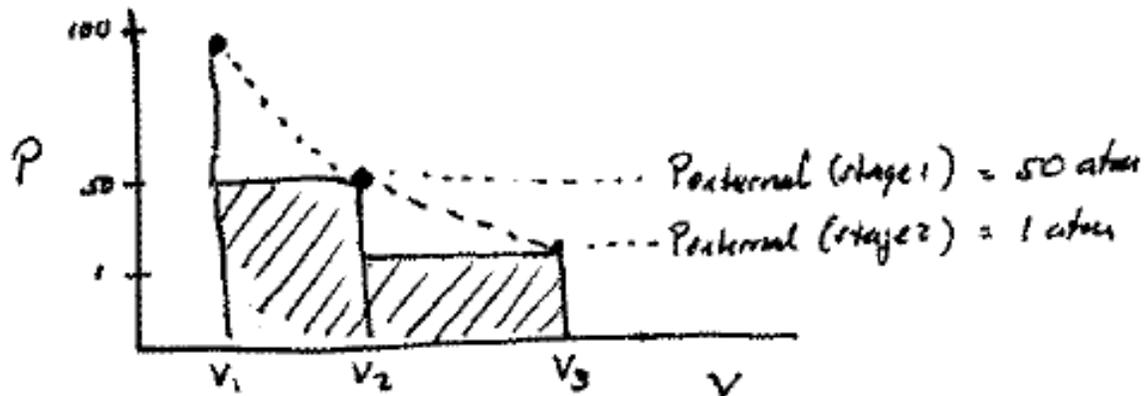
Although the gas is taken out of equilibrium during the expansion, if we pause long enough, it will equilibrate again at the ambient temperature T and at a pressure $P_2 = 50$ atm. In the second stage let us expand from $P_2 = 50$ atm against a constant external pressure of 1 atm. The work for this stage is

$$\begin{aligned}
 W_2 &= P_{\text{external}} (V_3 - V_2) \\
 &= P_{\text{external}} \left(\frac{nRT}{P_{\text{external}}} - \frac{nRT}{P_2} \right) \\
 &= nRT \left(\frac{P_{\text{external}}}{P_{\text{external}}} - \frac{P_{\text{external}}}{P_2} \right) \\
 &= nRT \left(1 - \frac{1}{50} \right) \\
 &= 0.98 nRT.
 \end{aligned}$$

The total work for the two stages is

$$\begin{aligned}
 W &= W_1 + W_2 \\
 &= 1.48 nRT \\
 &= 14.8 RT
 \end{aligned}$$

for $n = 10$ moles. Even though the final state of the gas is the very same state which was reached in Example 1, namely a final pressure of 1 atm and a temperature T , the work performed on the surroundings is larger by roughly 50%. This can be understood by looking at a graph of pressure versus volume. There are three



equilibrium points on the graph, one at $(V_1, P_1 = 100 \text{ atm})$ representing the initial state of the system, the second at $(V_2, P_2 = 50 \text{ atm})$ representing the state of the system at the end of stage 1, and the third at $(V_3, P_3 = 1 \text{ atm})$ representing the state of the system at the end of stage 2. The equation of state

$$P = \frac{nRT}{V}$$

applies for these three points, and therefore they lie on the isotherm connecting (V_1, P_1) to (V_3, P_3) . We should emphasize that, in order to cause the piston to expand, at each stage, we must *lower* external the pressure so that it is below the pressure of the system. Recall that in the first stage,

$$P_{\text{external (stage 1)}} = 50 \text{ atm},$$

which is certainly lower than the initial equilibrium pressure of the gas, i.e.

$$P_{\text{external (stage 1)}} < 100 \text{ atm} = \frac{nRT}{V_1}.$$

In the second stage

$$P_{\text{external (stage 1)}} = 50 \text{ atm}$$

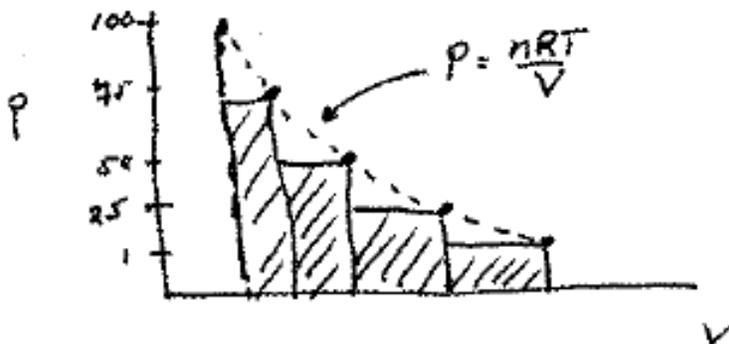
which is less than the equilibrium pressure at the start of the second stage, i.e.

$$P_{\text{external (stage 2)}} < 50 \text{ atm} = \frac{nRT}{V_2}.$$

Since the work in each stage is performed against a constant external pressure, it is given by the area of the shaded rectangles. Comparing this PV graph with the corresponding diagram in Example 1, it is clear that the area will be larger when the expansion is carried out in two stages.

Example 4:

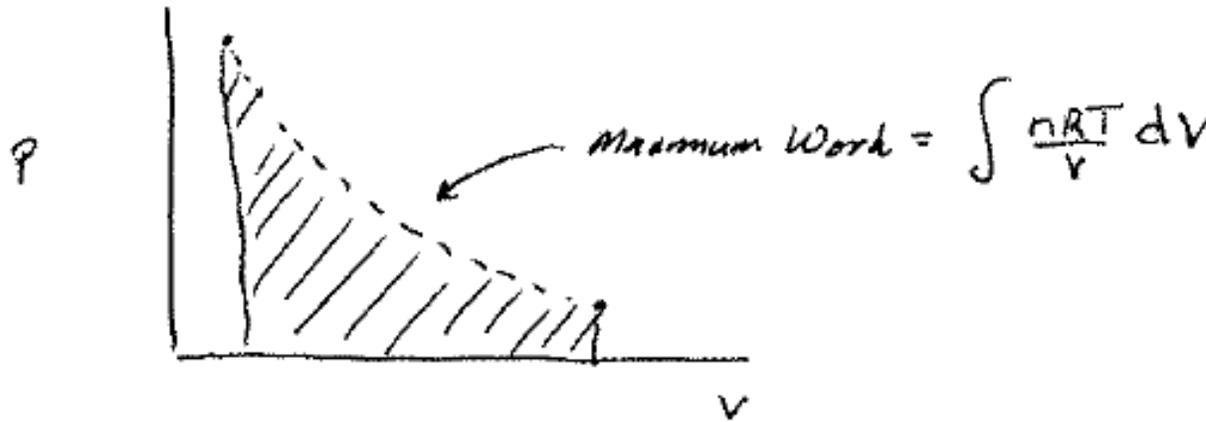
Let us suppose that we carry out the same isothermal expansion in 4 stages, first lowering the external pressure to 75 atm, then lowering the external pressure to 50 atm, then lowering the external pressure to 25 atm, and finally lowering the external pressure to 1 atm. As before, at the end of each stage we will pause to allow the gas in the cylinder to return to equilibrium. There are then 5 equilibrium points which can be located on a PV isotherm, as shown below.



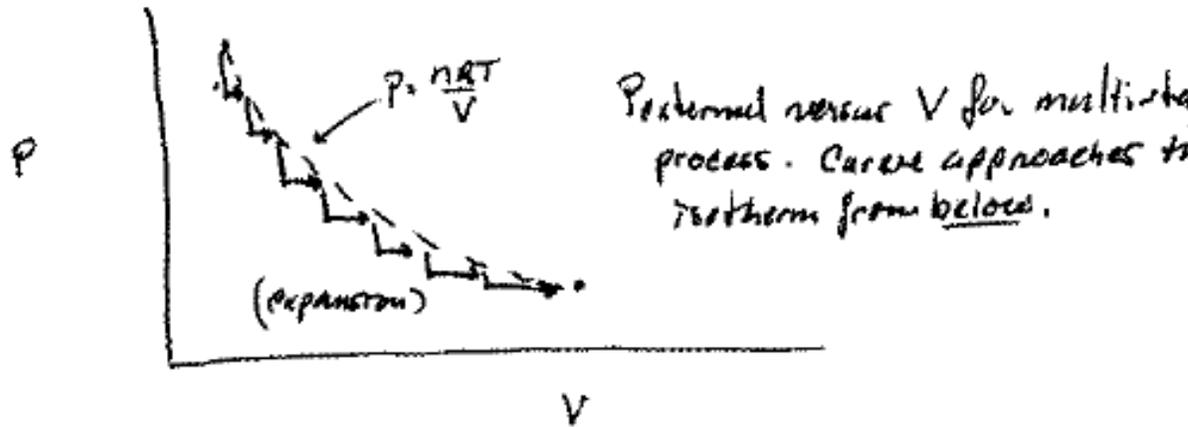
The work performed is indicated by the shaded region, and it is clearly larger than the work which was harvested in the 2-stage expansion. You will want to go through the math to convince yourself that the total work for the 4-stage expansion will be

$$W = 19.83 RT$$

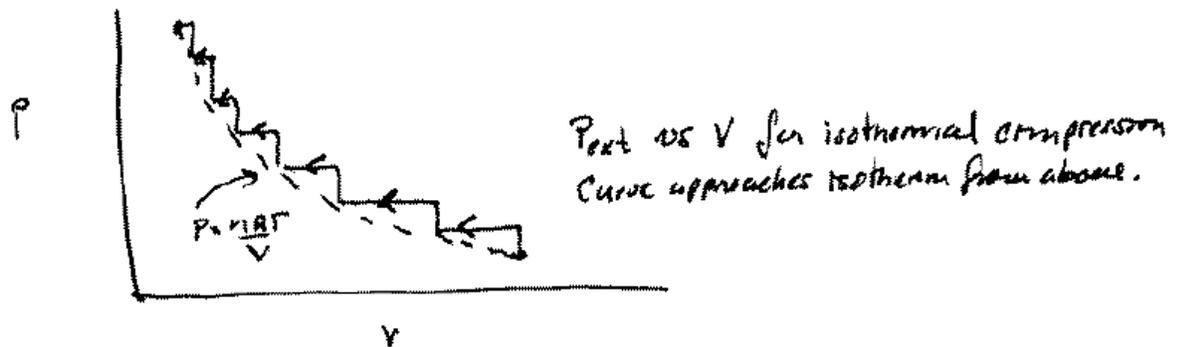
What will the work be if the isothermal expansion is carried out in 8 stages? In 16 stages? By imagining how the work for a multi-stage expansion would be indicated on a PV diagram, it should be obvious that the work increases with the number of stages, reaching a maximum as the number of stages goes to infinity. In this limit, the difference between the external pressure and the equilibrium pressure for each stage is so small that we may as well replace P_{external} by the pressure $P = nRT/V$ along the equilibrium isotherm. Thus the *maximum* work which can be performed in the expansion is given by the area under the isotherm,



$$\begin{aligned}
 W_{\max} &= \int_{\text{initial}}^{\text{final}} P_{\text{external}} dV \\
 &= \int_{\text{initial}}^{\text{final}} P dV \\
 &= \int_{\text{initial}}^{\text{final}} \frac{nRT}{V} dV \\
 &= nRT \int_{\text{initial}}^{\text{final}} \frac{dV}{V} \\
 &= nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}} \\
 &= nRT \ln \frac{\left(\frac{nRT}{P_{\text{final}}}\right)}{\left(\frac{nRT}{P_{\text{initial}}}\right)} \\
 &= nRT \ln \frac{P_{\text{initial}}}{P_{\text{final}}} \\
 &\Rightarrow 10RT \ln \frac{100}{1} = 46.1 RT
 \end{aligned}$$



In the examples above we have not discussed how much work would be required to return the system to its initial state. We have already seen in Example 2 that the work which must be performed by the surroundings on the system for recompression of the gas is actually larger than the work performed by the gas on the surroundings in the initial expansion. Consequently, for a cycle which returns the gas to its initial state, the *net* work performed by the system is negative. The same is true for a multi-stage processes, except that the difference between the work performed *on* the system in compression and the work performed *by* the system in expansion becomes smaller as the number of stages increases. Why must the work to compress the gas be larger than work done by the gas in expansion? In order to move the piston inward, the external pressure must be *increased* above the equilibrium gas pressure at each stage. Thus for compression, the series of rectangles representing the work on the PV diagram will always lie above the PV isotherm.



Thus, just as we may write

$$W_{\text{expansion}} \leq \int_{100 \text{ atm}}^{1 \text{ atm}} PdV$$

we may also write

$$-W_{\text{compression}} \geq \int_{100 \text{ atm}}^{1 \text{ atm}} PdV$$

Here we have recognized that the work done *by* the system is negative during compression, and so we have put in the negative sign so that the inequality makes sense. The total work for a cycle which returns the gas to its initial state is therefore

$$\begin{aligned} W_{\text{cycle}} &= W_{\text{expansion}} + W_{\text{compression}} \\ &\leq 0 \end{aligned}$$

The equality is only to be taken when both the expansion and the compression follow the isotherm, i.e. when they are carried out in an infinite number of stages.

In the infinite stage process, the work done on expansion is equal in magnitude and opposite in sign to the work done on compression. Such a process is called a *reversible process*, since the expansion and compression take place along the same (equilibrium) path on the PV diagram. A reversible process is only a hypothetical process. If we were to really follow a path in, say, an expansion, where the external pressure is dropped below the system pressure by an infinitesimal amount, then the acceleration of the piston at each stage would also be infinitesimal, and as a result, the time taken between each infinitesimal stage would be finite. In such a case, the total time for a process which consists of an infinite number of steps would be infinite, and therefore we must conclude that such a process can never actually take place.

This is a rather general principle; processes that actually take place (in a finite amount of time) must be induced by reducing some external variable (like pressure, or temperature) below the system value by a fixed amount. But as we have illustrated above for the case of the isothermal expansion, this will take the system out of equilibrium, and as a result, the work done in one direction will no longer be equal to the work done in the other direction. The same applies to heating; when heat is caused to flow by a difference in temperature between system and surroundings, the heat added to take the system in one direction will not necessarily be equal to the heat added to restore the system to its initial state. Such processes are called *irreversible*.

The relation between reversibility of a process and the time it takes for a process to occur is intuitively obvious, but it sounds rather profound when stated as follows: Any process that actually occurs in a finite amount of time, i.e. any process in nature that takes place *spontaneously*, is necessarily an *irreversible* process. As we will see later on, this relationship between spontaneity and irreversibility is an integral part of the postulate that is called the *second law of thermodynamics*.

Before closing, let us return to our example above in the context of the first law,

$$\Delta U = Q - W$$

Since U is a state variable, it returns to its initial value on the completion of any cycle. This means that

$$\Delta U_{\text{cycle}} = 0.$$

It follows that

$$Q_{\text{cycle}} = W_{\text{cycle}}$$

From the inequality above, $W_{\text{cycle}} \leq 0$, this means that the heat added to the system from the surroundings in the cycle is also such that

$$Q_{\text{cycle}} \leq 0$$

Alternatively, the heat that is dumped into the surroundings from the system will be such that

$$Q_{\text{cycle (surroundings)}} \geq 0$$

The inequality expresses two possibilities; first if the cycle is carried out reversibly, then

$$Q_{\text{cycle (surroundings)}} = 0;$$

and no heat is dumped into the surroundings; on the other hand, for the irreversible cycle,

$$Q_{\text{cycle (surroundings)}} > 0.$$

The implication is that we must dump heat (exhaust) into the surroundings in order to carry out a cyclic process (one that restores a system to its original state) in any finite amount of time. The exhaust heat can be reduced by carrying out the process as reversibly as possible, but this implies a very slow process - one that takes a long time. For most processes, we can't afford to wait forever, and/or we lack patience, and so we stuck with heating up the surroundings.

Suppose that there were no surroundings available in which to dump the exhaust heat. The system could be insulated, for example. Wouldn't this make it impossible to carry out a cyclic process (in a finite amount of time) that would return our system to its original state?