THERMODYNAMICS

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QUASI-STATIC PROCESS

Think about a gas that's all balanced and cozy with its surroundings. Its pressure matches the outside pressure, and its temperature is the same as what's around it.

Now, imagine that the outside pressure suddenly drops, like when you lift a weight off a piston. The piston will zoom outwards. During this change, the gas goes through states where it's not balanced. In these not-so-happy states, you can't pin down a specific pressure or temperature.

If the gas and its surroundings have different temperatures, they'll quickly swap heat, and the gas will pass through not-balanced states. But with time, the gas will chill out and reach a balanced state with a clear temperature and pressure, just like its surroundings.

When a gas freely expands into a vacuum or if a mix of gases explodes, it also goes through these not-so-balanced states.

Dealing with non-balanced states of a system can be tricky. So, we like to imagine a special, slow process where at each step, the system is balanced, like a perfect equilibrium. This process is super slow, which is why we call it "quasi-static" (almost static).

In a quasi-static process, the system changes its properties (like pressure, temperature, and volume) really, really slowly so that it's always in balance with its surroundings. At each step, the difference in pressure between the system and the outside is incredibly tiny. The same goes for temperature.

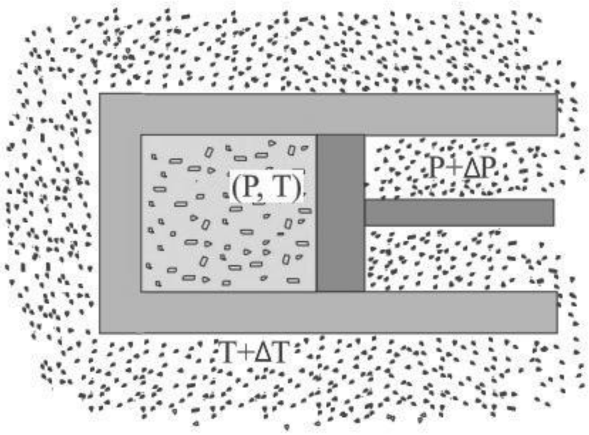


Fig. During a quasi-static process, the temperature of the surroundings and the external pressure are just a tiny bit different from the temperature and pressure of the system.

To move a gas from one state (P, T) to another (P ′, T ′) using a quasi-static process, we make a tiny change in the external pressure, let the system catch up with the surroundings' pressure, and keep doing this super slowly until the system reaches the new pressure, P ′. The same goes for temperature. We introduce a really small temperature difference between the system and the surroundings, and by using reservoirs with gradually different temperatures, the system slowly reaches the new temperature, T ′.

When a process keeps the system's temperature steady, it's called an isothermal process. For example, if you have a gas in a metal cylinder sitting in a big tank with a fixed temperature, and the gas expands, it's an isothermal process. The heat moving from the tank to the system doesn't really change the tank's temperature because it can hold a lot of heat.

In isobaric processes, the pressure stays the same, and in isochoric processes, the volume stays the same. And if the system is all wrapped up and can't exchange heat with the surroundings, it's an adiabatic process.

Type of processes	Feature
Isothermal	Temperature constant
Isobaric	Pressure constant
Isochoric	Volume constant
Adiabatic	No heat flow between the system and the surroundings ($\Delta Q = 0$)

Isothermal process

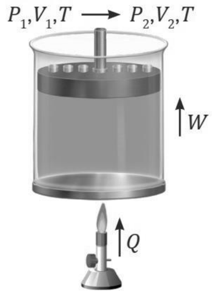
This is when something stays at the same temperature, so it doesn't get hotter or colder (the temperature doesn't change). But the pressure and size of that thing can still change as it goes through different stages.

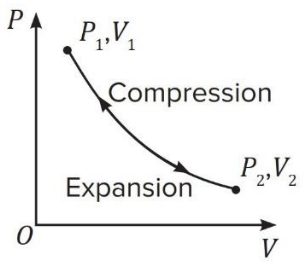
Equation of state: PV = constant
The graph of the P-V curve looks like a curvy shape called a hyperbola, and we call it an isotherm.

Slope of the isotherm: $\left(\frac{dP}{dV}\right)_T = -\frac{P}{V}$

Heat can move between the system and its surroundings.

To keep things at the same temperature, the process needs to be very slow and careful, like a snail, and we call this "isothermal."





Work done in an isothermal process

$$W = \int_{V_1}^{V_2} P\,dV$$

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

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

$$= nRT \left[\ln(V)\right]_{V_1}^{V_2}$$

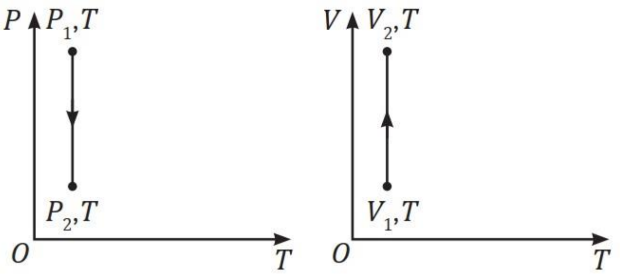
$$\Rightarrow W = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow W = nRT \ln\left(\frac{P_1}{P_2}\right)$$

$W > 0$ (Positive) for $V_2 > V_1$ (Expansion)

$W < 0$ (Negative) for $V_2 < V_1$ (Compression)

P-T and V-T plots for an isothermal expansion

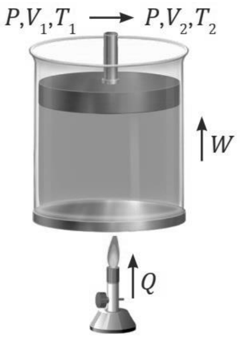


Isobaric process

This is when the system's size and heat can change, but the pressure always stays the same, like a fixed number that doesn't move.

Equation of state: $V \propto T$ or, $\frac{V}{T} = \text{Constant}$

The slope of the P-V plot is zero.



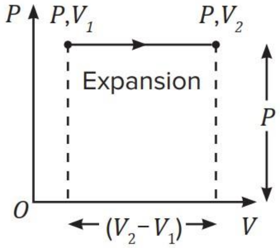
Work done in an isobaric process

$$W = \int_{V_1}^{V_2} P\,dV$$

$$= P\int_{V_1}^{V_2} dV$$

$$\Rightarrow W = P\left(V_2 - V_1\right)$$

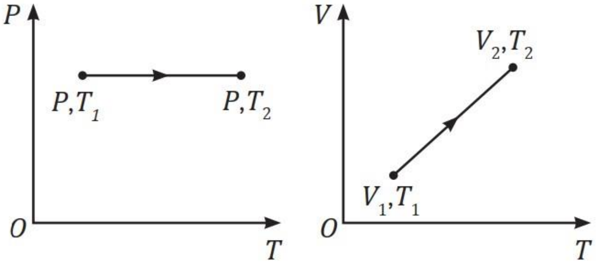
$$\Rightarrow W = nR\left(T_2 - T_1\right)$$



W > 0 (Positive) for V2 - V1 > 0 (Expansion)

W < 0 (Negative) for V2 - V1 < 0 (Compression)

P-T and V-T plots for an isobaric expansion



Isochoric process

This is a type of process where the system's size doesn't change (it stays the same), but the pressure and temperature of the system can still change as it goes through different stages.

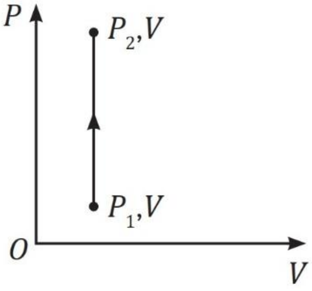
Equation of state: P ∝ T or, $\frac{P}{T}$ = Constant

The plot of P-V is a straight line parallel to the y-axis (P-axis).

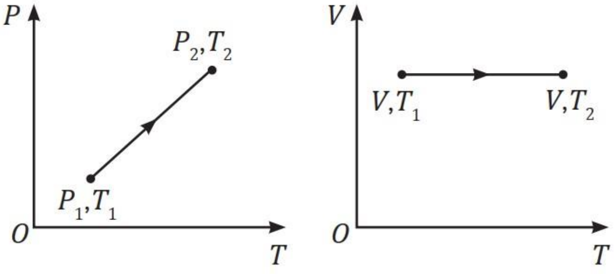
Work done in an isochoric process

$$W = \int_{V_2}^{V_1} Pdv$$

$$= 0 \text{ (Since } dv = 0\text{)}$$



P-T and V-T plots for an isochoric expansion



Cyclic Process

This is a thermodynamic process where the system goes through some changes and then ends up back where it started. It's like taking a round trip with the system, going through different steps, and eventually coming back to the beginning.

Imagine a thermodynamic system starting at point 1 on a chart. It moves from point 1 to point 4, but it takes two different paths: one where the pressure stays the same (1 ⟶ 2 and 3 ⟶ 4), and another where the volume stays the same (2 ⟶ 3 and 4 ⟶ 1). Then, it goes back from point 4 to where it started using a path where the volume stays the same again. This whole setup of the system moving through these two different paths repeatedly is called a cyclic process, like a repeating pattern.

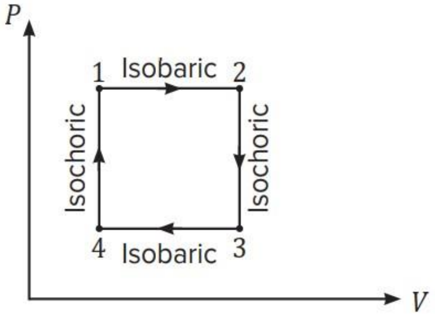
Recall that internal energy (U) is a state function; therefore, in this cyclic process,

$$\Delta U_{cyclic} = \Delta U_{1\to2} + \Delta U_{2\to3} + \Delta U_{3\to4} + \Delta U_{4\to1}$$

$$= (U_2 - U_1) + (U_3 - U_2) + (U_4 - U_3) + (U_4 - U_1)$$

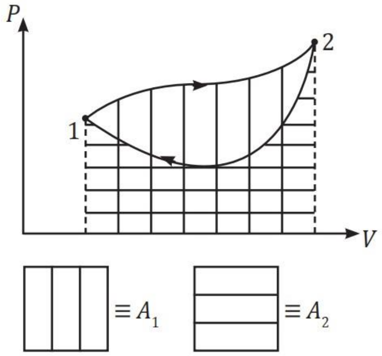
Or

$$\Delta U_{cyclic} = 0$$



Work done in cyclic process

Let's look at another case where we have a cycle between two points, 1 and 2. When the system goes from 1 → 2, it's expanding, and when it goes from 2 → 1, it's compressing. We can figure out the work done by looking at the area under the curve on a graph where pressure and volume are shown. When the area is above the volume axis, we consider it positive for expansion, and when it's below the volume axis, we consider it negative for compression.



Hence, the net work done by the gas,

$W_{cyclic} = W_{1\rightarrow2} + W_{2\rightarrow1}$

Or

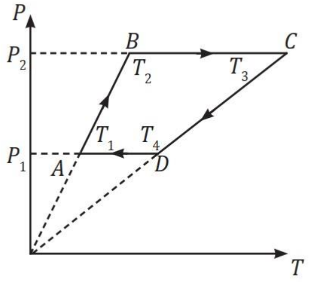
$W_{cyclic} = A_1 + A_2$

$W_{cyclic} =$ Area bounded by the cycle on the P-V plot

For a conventional cyclic process (P on the y-axis and V on the x-axis),

$W_{cyclic} > 0$, For a clockwise cycle

$W_{cyclic} < 0$ For an anti-clockwise cycle



Example.

Look at this curve that shows pressure and temperature for a cycle. To figure out how much work the gas does during this process, we need to know the number of moles of the gas, which we call "n."

Solution.

As shown in the figure, the cyclic process consists of two isobaric processes (B⟶C and D⟶ A)

And two isochoric processes (A⟶B and C⟶D).

The net work done by the gas (W cycle) is,

$W_{cycle} = W_{A \rightarrow B} + W_{B \rightarrow C} + W_{C \rightarrow D} + W_{D \rightarrow A}$

$$\Rightarrow W_{cycle} = 0 + P_2 (V_3 - V_2) + 0 + P_1 (V_1 - V_4)$$

$$\Rightarrow W_{cycle} = nR (T_3 - T_2) + nR (T_1 - T_4)$$

$$\Rightarrow W_{cycle} = nR (T_1 - T_2 + T_3 - T_4)$$

Adiabatic Process

This is a process where heat doesn't move in or out, meaning there's no heat transfer happening ($dQ = 0$).

From the ideal gas equation,

$PV = nRT$

On taking differential w.r.t. on both the sides, we get,

$$\frac{d(PV)}{dT} = \frac{d(nRT)}{dT}$$

$$\Rightarrow P\frac{dV}{dT} + V\frac{dP}{dT} = nR$$

$$\Rightarrow \frac{PdV + VdP}{R} = ndT \quad .....(i)$$

From the first law of thermodynamics,

$dQ = dU + dW$

Or

$$nC_n dT = nC_V dT + PdV$$

$$\Rightarrow nC_V dT + PdV = 0 \quad (\because\ dQ = 0 \text{ for an adiabatic process})$$

$$\Rightarrow C_V\left[\frac{PdV + VdP}{R}\right] + PdV = 0 \quad (\text{From equation } (i))$$

$$\Rightarrow C_V\left[PdV + VdP\right] + RPdV = 0$$

$$\Rightarrow C_V\left[PdV + VdP\right] + (C_P - C_V)PdV = 0 \quad (\because\ C_P - C_V = R)$$

$$\Rightarrow C_V VdP + C_P PdV = 0$$

$$\Rightarrow \frac{dP}{P} = -\left(\frac{C_P}{C_V}\right)\frac{dV}{V}$$

$$\Rightarrow \frac{dP}{P} = -\gamma\frac{dV}{V}$$

On integrating both the sides (indefinite), we get,

$$\int \frac{dP}{P} = -\gamma \int \frac{dV}{V}$$

$$\Rightarrow \ln P = -\gamma \ln V + c$$

$$\Rightarrow \ln P + \gamma \ln V = c$$

$$\Rightarrow PV^{\gamma} = \text{Constant}$$

γ is also known as the adiabatic exponent of the gas.

There are two ways to perform an adiabatic process.

- This process happens in a closed area with walls that don't let heat in or out.
- This process happens very quickly, so fast that there's no time for any heat exchange to occur.

For the adiabatic process of an ideal gas,

PV^{γ}= Constant

$$\Rightarrow \left(\frac{nRT}{V}\right)V^{\gamma} = \text{Constant}$$

$$\Rightarrow TV^{\gamma-1} = \text{Constant}$$

Similarly,

$$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{Constant}$$

$$\Rightarrow P^{1-\gamma}T^{\gamma} = \text{Constant}$$

Work Done in an Adiabatic Process

We have, for adiabatic process

$PV^{\gamma} = P_1{V_1}^{\gamma} = P_2{V_2}^{\gamma} = k$

The work done in an adiabatic process is,

$$W = \int_{V_1}^{V_2} P dV$$

$$= \int_{V_1}^{V_2} \frac{k}{V^{\gamma}} dV$$

$$= k\int_{V_1}^{V_2} \frac{1}{V^{\gamma}} dV$$

$$= k\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$= k\left[\frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}\right]$$

$$= \frac{kV_2^{1-\gamma} - kV_1^{1-\gamma}}{1-\gamma}$$

$$= \frac{\left(P_2V_2^{\gamma}\right)V_2^{1-\gamma} - \left(P_1V_1^{\gamma}\right)V_1^{1-\gamma}}{1-\gamma}$$

$$W = \frac{P_2V_2 - P_1V_1}{1-\gamma} \text{ or } \frac{P_1V_1 - P_2V_2}{\gamma-1}$$

$$W = \frac{nR\left(T_2 - T_1\right)}{1-\gamma}$$

Alternatively,

$$W = -\Delta U$$

$$\Rightarrow W = -nC_V\Delta T$$

$$\Rightarrow W = -n\left[\frac{R}{\gamma-1}\right]\left(T_2 - T_1\right)$$

$$\Rightarrow W = \frac{nR\left(T_2 - T_1\right)}{1-\gamma}$$

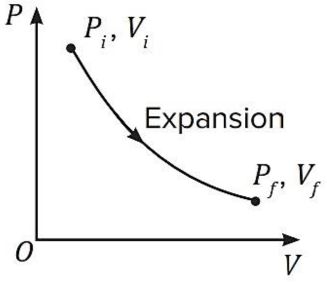
Change in temperature

The formula for the work done in an adiabatic process is,

$$W = \frac{nR(T_i - T_f)}{\gamma - 1}$$

For expansion, the work done is positive. Therefore, Tf < Ti.

For compression, the work done is negative. Therefore, Tf > Ti.



Example.

An ideal gas having initial pressure P, volume V, and temperature T is allowed to expand adiabatically until its volume becomes 5.66 V, while its temperature falls to $\frac{T}{2}$

(a) how many degrees of freedom do the gas molecules have?

(b) Obtain the work done by the gas during the expansion as a function of the initial pressure P and volume V.
(Given, ln (5.66) = 2.5 ln 2)

Solution.

(a) Given,

$$\text{In}\,(5.66) = 2.5\ \text{In}\,(2)$$
$$= \text{In}\,(2^{2.5})$$
$$= \text{In}\left(\sqrt{32}\right)$$
$$\Rightarrow 5.66 = \sqrt{32} = 4\sqrt{2}$$

The change of state of the system through an adiabatic process is as follows:

$$(\mathrm{P}, \mathrm{V}, \mathrm{T}) \xrightarrow{\text{Adiabatic}} \left(\mathrm{P}', 4\sqrt{2}\mathrm{V}, \frac{\mathrm{T}}{2}\right)$$

By using the combined gas equation for both the states, we get,

$$\frac{PV}{T} = \frac{P' \times 4\sqrt{2}V}{\left(\frac{T}{2}\right)}$$

$$\Rightarrow P' = \frac{P}{8\sqrt{2}}$$

For an adiabatic process,

$$PV^{\gamma} = P'V'^{\gamma}$$

$$\Rightarrow PV^{\gamma} = \frac{P}{8\sqrt{2}}\left(4\sqrt{2}V\right)^{\gamma}$$

$$\Rightarrow 2^{\frac{7}{2}} = 2^{\frac{5}{2}\gamma}$$

$$\Rightarrow \gamma = \frac{7}{5}$$

(b)
$$W = \frac{P_2V_2 - P_1V_1}{1-\gamma}$$

$$\Rightarrow W = \frac{\left(\frac{P}{8\sqrt{2}}\right)\left(4\sqrt{2}\right) - PV}{1-\frac{7}{5}}$$

$$\Rightarrow W = \frac{-\frac{PV}{2}}{-\frac{2}{5}}$$

$$\Rightarrow W = \frac{5}{4}PV$$

Standard Thermodynamic Processes

Here are the common types of processes in thermodynamics:

(i) Isothermal (ii) Isobaric (iii) Isochoric (iv) Adiabatic

Type of standard thermodynamic process	Characteristic
Isothermal	Temperature remains constant (dT = 0)
Isobaric	Pressure remains constant (dP = 0)
Isochoric	Volume remains constant (dV = 0)
Adiabatic	Heat transfer is zero (δQ = 0)