

Does U depend on T and V ? Recall that in general,

$$\Delta U = q_V + W = C_V dT + PdV$$

The internal energy of an ideal gas is a function of T , but is not a function of V . Volume change increases or decreases U by changing T . In other words:

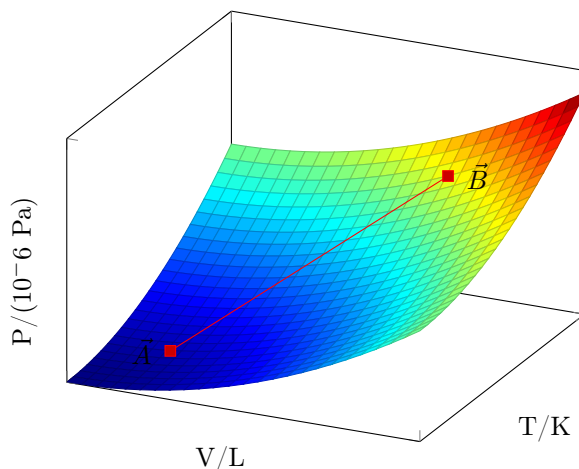
$$\Delta U = f(T) \quad \Delta U \neq f(V) \quad \Delta U \neq f(P) \quad \frac{\partial U}{\partial T} = 0$$

For isothermal processes, i.e. when $\Delta T = 0$,

$$\Delta U = 0 \quad q_T = -W_T$$

If the rate of change of the macroscopic variables is negligibly small, the system passes through a succession states of internal equilibrium as it goes from the initial to final states.

All combinations of P , V and T are consistent with 1 mol of an ideal gas lie on the colored surface. Say we consider the path $\vec{A} = \begin{pmatrix} P_A \\ V_A \\ T_A \end{pmatrix}$ to $\vec{B} = \begin{pmatrix} P_B \\ V_B \\ T_B \end{pmatrix}$.



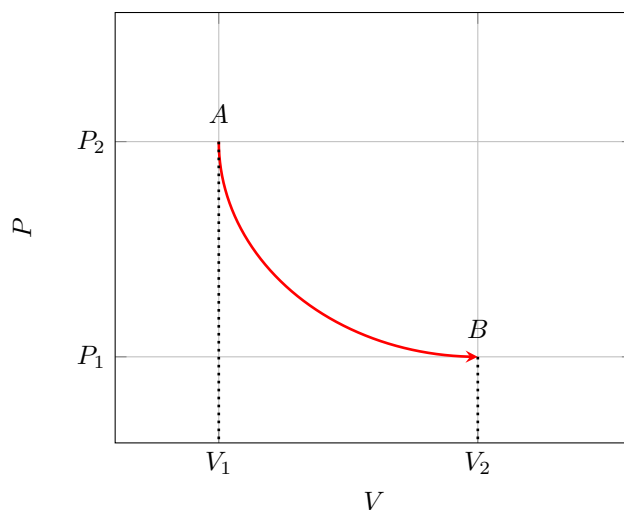
Classes of Quasi-Static Processes:

1. Reversible: If an infinitesimal opposing change in the variable that drives the process that causes reversal in the direction of the process.
2. Irreversible: If an infinitesimal change in driving variable does not change the direction of the process.

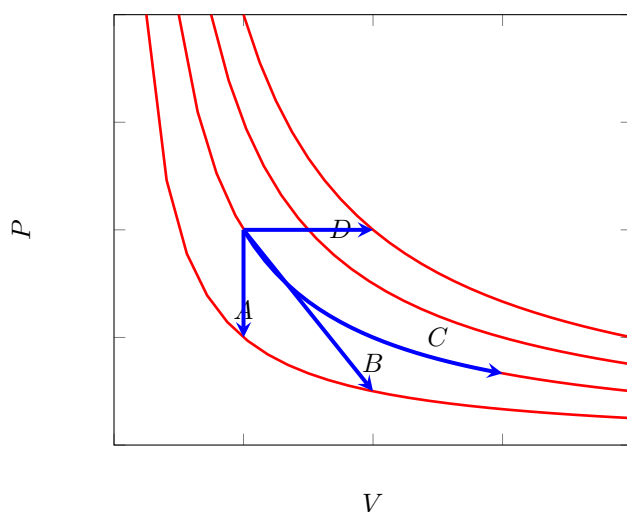
If the rate process is too fast, molecules can't keep up to keep system homogeneous. For this course, we will assume quasi-static processes so can assign single value of P , V , T and n for system and surroundings.

PV-DIAGRAMS

PV -diagrams are used when the *pressure* and *volume* are known at each step of the process. The state of the gas at each step can be plotted on a graph called a PV -diagram. This allows us to visualize the process through which the gas is progressing. The curve is called the path.



Isotherms are plots of pressure vs volume of gas at the same temperature. On a PV -diagram, it is a hyperbola.



If $PV = nRT$ or $P = \frac{nRT}{V}$, for an isothermal process, T is constant and so nRT is constant. That is,

$$P = \beta \frac{1}{V} \Leftrightarrow P \propto \frac{1}{V}$$

How can the amount of work done by gas vary?

1. Have a gas expanding against a vacuum meaning no weight:

$$P_{ext} = 0, -P_{ext}\Delta V = 0 \Rightarrow W = 0$$

2. Have a gas expanding against a mass so gas expands against a constant external pressure:

$$W = -P_{ext}\Delta V$$

For example, if $P_{ext} = 3$ atm and $P_{int} = 10$ atm, the gas will only expand until $P_{int} = 3$ atm then the expansion will stop.

Example 1. 3.00 moles of an ideal gas at 27.0°C expand isothermally from an initial volume of 20.0 L to a final volume of 60.0 L. Calculate W for this process for expansion against a constant external pressure of 1.00 atm.

Solution 1. Given $V_1 = 20.0$ L, $V_2 = 60.0$ L, and $P = 1.00$ atm, the work W for an expansion against a constant pressure is:

$$W = -P_{ext}\Delta V = -(1.00) \times (40.0) = -40 \text{ L atm}$$

We convert to J using the conversion factor $1 \text{ L atm} = 101.325 \text{ J}$

$$W = -40 \times 101.325 = -4053 \text{ J}$$

as desired. □

Question 1. *Is it possible to have the system perform a greater amount of work for the same increase in volume?*

Answer 1. Yes!

Example 2. *Suppose that the weight on the piston is made up of an infinitesimal number of small weights each of which contribute to a total external pressure of 10 atm*

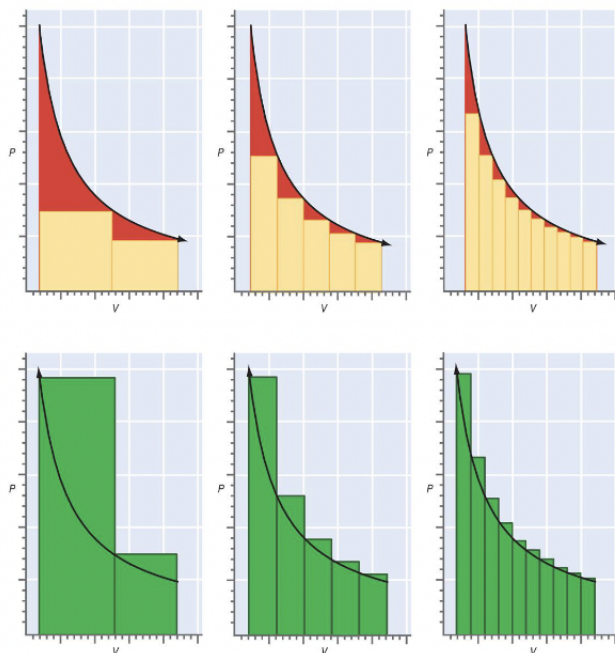
Solution 2. So this implies that $P_{int} = P_{ext}$. Removing one weight will decrease P_{ext} by an infinitesimal amount, so $P_{int} > P_{ext}$ and gas will expand by an infinitesimal amount until $P_{int} = P_{ext}$.

We can continue to do this by progressively removing one weight at a time...gas expands by an infinitesimal amount with removal of each weight.

In a reversible path, the system remains infinitely close to the equilibrium! Integration is needed when P_{ext} changes during the process. For a reversible path, let dP be the infinitesimal change of P , and let T be constant. Then

$$W = - \int_{V_1}^{V_2} P_{ext} dV = - \int_{V_1}^{V_2} (P - dP) dV = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \log \left(\frac{V_2}{V_1} \right)$$

Work done is equal to the area under PV curve.



It is an *expansion* if the system is doing work on the surroundings.

$$|W_{reversible}| \geq |W_{irreversible}|$$

It is a *compression* if the surroundings are doing work on the system.

Example 3. Recall in the given values in Example 1. Calculate W for this process for a reversible expansion.

Solution 3. Given $V_1 = 20.0$ L, $V_2 = 60.0$ L, and $P = 1.00$ atm, then

$$W = -(3.00)(0.08206)(300) \log \left(\frac{60.0}{20.0} \right) = 81.1370 \times 8.314 = -674.57 \text{ J}$$

First Law Summary

$$\Delta U = U_2 - U_1 = q + W$$

For a closed system with no phase changes and no chemical reactions, heat applied or removed from the system:

$$q = \int_{T_1}^{T_2} C dT = \int_{T_1}^{T_2} m\bar{c} dT$$

If C is constant in the temperature range between T_2 and T_1 is $q = m\bar{C}\Delta T$. The work done by the system is

$$W = - \int_{V_1}^{V_2} P_{ext} dV$$

When P_{ext} is constant,

$$\Delta U = U_2 - U_1 = q + W = m\bar{C}\Delta T - P_{ext}\Delta V$$

- Compression: Work done on or by the system at constant external pressure:

$$U_2 - U_1 = m\bar{C}\Delta T - P_{ext}\Delta V$$

- No volume change: $\Delta V = 0$,

$$W = 0 \quad U_2 - U_1 = q = C_V \Delta T$$

- No heat exchange at constant external pressure:

$$q = 0 \quad U_2 - U_1 = W = -P_{ext}\Delta V$$

- No temperature change: $\Delta U = 0$,

$$W = -q = nRT_1 \log \left(\frac{P_2}{P_1} \right) = nRT_1 \log \left(\frac{V_1}{V_2} \right)$$

1. Work is a form of energy transfer...another form is heat.
2. In an isothermal expansion, maximum amount of work is done by a reversible process.
3. Expansion only occurs when there is a pressure difference.
4. The amount of work done depends on how the process is carried out, this means work is not a state function as it is path dependent.