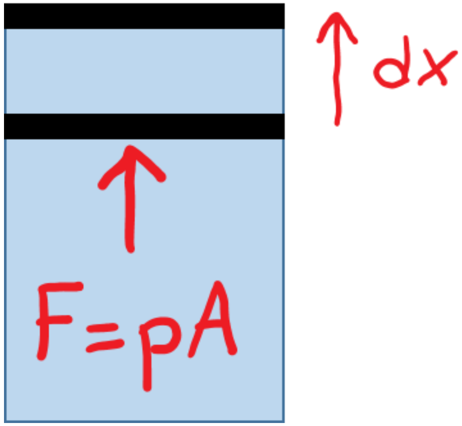
Lecture 29: 1st Law of Thermodynamics

- thermodynamic work
- 1st law of Thermodynamics
- equation of state of the ideal gas
- Isochoric, isobaric, and isothermal process in ideal gas

Thermodynamic work



$$dW = Fdx = pAdx = pdV$$

$$\boxed{W = \int_i^f p(V,T)dV}$$

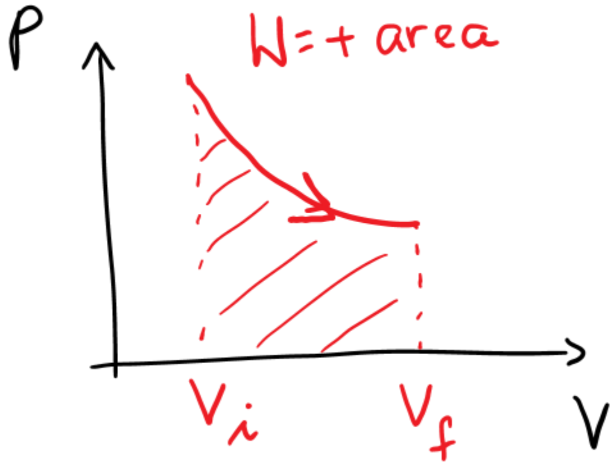
work done **by** the gas

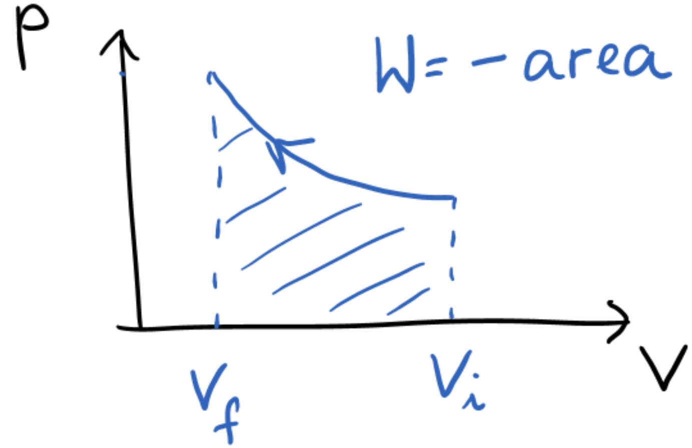
Work and p-V curve

$$W = \int_i^f p(V,T)dV$$

work done **by** the gas
$\Longrightarrow$ area under the $p - V$-curve

$W > 0$ if gas **expands** ($\Delta V > 0$)
$W < 0$ if gas is **compressed** ($\Delta V < 0$)





First Law of Thermodynamics

The internal energy of a system can change:

- Heat flow in or out of system
- Work done on or by gas

$$\boxed{\Delta U = Q - W}$$

Q: net heat flowing into the system
W: work done by the system

ΔU is completely determined by initial and final values of the state variables
(even though W and Q depend on the process!)

Internal energy

Internal energy U of the system
= kinetic energies of particles
+ potential energy of interaction

Value of U depends on state of system only.

State is characterized by state variables such as:
temperature, pressure, volume, phase

Ideal gas

- particles do not interact with each other
- only elastic collisions between particles and with walls

Real gas can be treated as ideal if:
low density, low pressure, high temperature

State variables are related by:

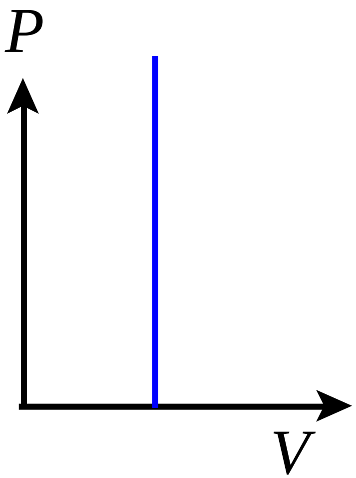
$$\boxed{pV = nRT}$$

n number of moles
R universal gas constant
R=8.315J/(mol· K)

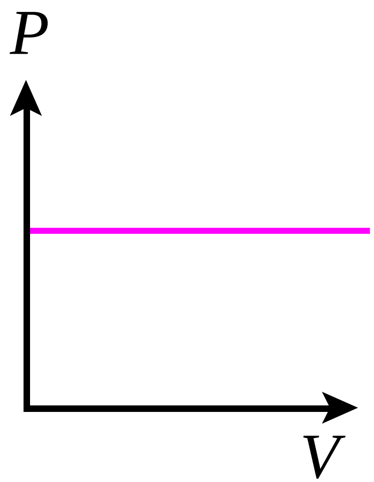
No interactions between particles
$\Longrightarrow U$ consists only of kinetic energies of particles
$\Longrightarrow U$ depends only on temperature: $U = U(T)$ *

* Only true for ideal gas!

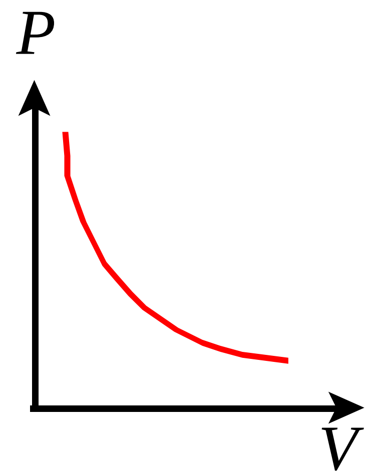
Important processes for the ideal gas



V=const.
isochoric



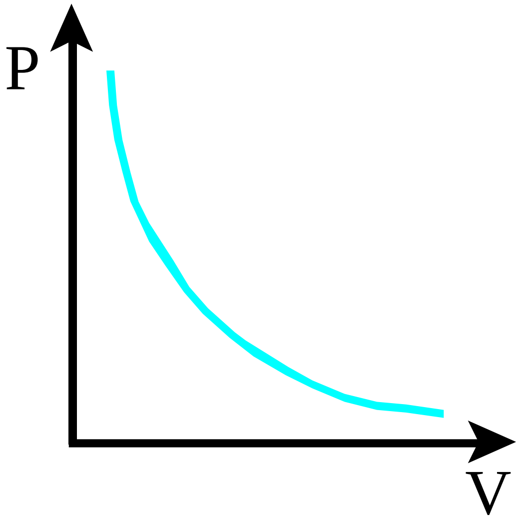
p=const.
isobaric



T=const.
isothermal

$$pV = nRT$$
$$p \sim \frac{1}{V}$$

Adiabatic Process



$Q = 0$

$pV^{\gamma} = const$

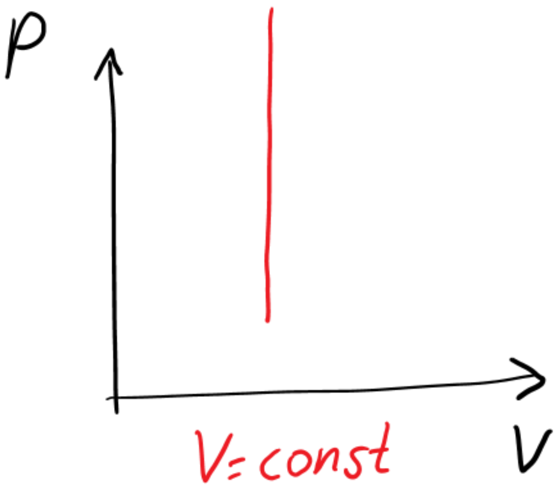
$\gamma = c_p/c_V$

$\gamma = 1.67\ (monoatomic)$

$or\ 1.40\ (diatomic)$

$\gamma > 1$ steeper than isothermal

Isochoric process for the ideal gas



$$W = \int p\,dV = 0$$

$$Q = nc_V \Delta T$$

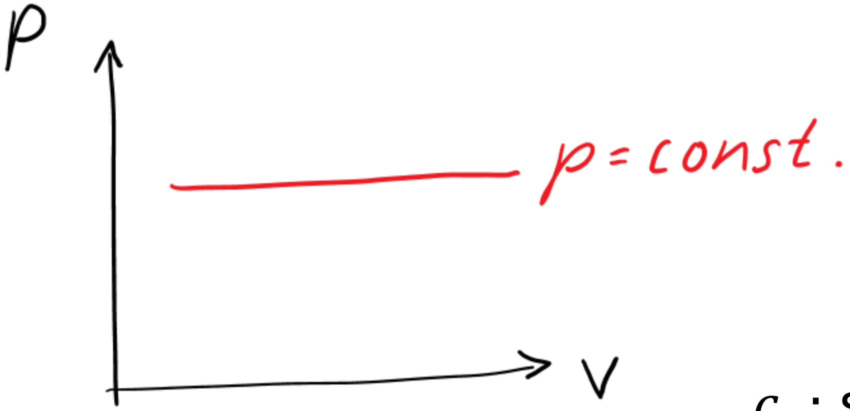
c_V: specific heat at constant volume

Monatomic: $c_V = \frac{3}{2}R$

Diatomic gas: $c_V = \frac{5}{2}R$

$$\boxed{\Delta U = Q - W = nc_V \Delta T}$$

Isobaric process for the ideal gas



$$W = \int p\, dV = p \int dV = p\Delta V$$

$$Q = n c_p \Delta T$$

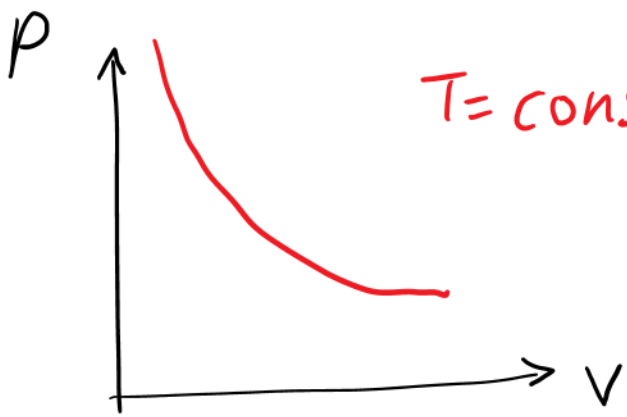
c_p: specific heat at constant pressure

Monatomic gas: $c_p = \frac{5}{2} R$

Diatomic gas: $c_p = \frac{7}{2} R$

$$\boxed{\Delta U = Q - W = n c_p \Delta T - p\Delta V}$$

Isothermal process for the ideal gas



$$W = \int p\, dV$$

$$pV = nRT$$

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

$$W = \int_i^f \frac{nRT}{V} dV = nRT \int_i^f \frac{dV}{V}$$

$$W = nRT\ ln \frac{V_f}{V_i}$$

$U = U(T)$. If $T = constant, U = constant$.

$\Delta U = 0$ in an isothermal process.

$$\boxed{\begin{aligned} \Delta U &= Q - W = 0 \\ Q &= W = nRT\ ln \frac{V_f}{V_i} \end{aligned}}$$

Isobaric vs isochoric process

Consider two process between same two temperatures:

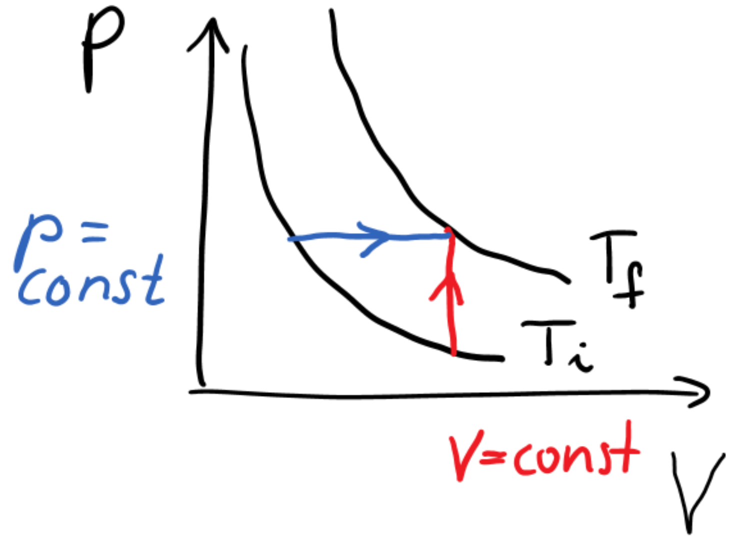
Isochoric: $\Delta U = nc_V \Delta T$

Isobaric: $\Delta U = nc_p \Delta T - p\Delta V$

$$nc_V \Delta T = nc_p \Delta T - p\Delta V$$

with $p\Delta V = nR\Delta T$:

$$\boxed{c_p - c_V = R}$$



To increase U by same amount as in isochoric process,
more Q needed for isobaric process because gas is doing work

Difference between c_V and c_p

$$\boxed{c_p - c_V = R}$$

Monatomic gas: $c_V = \frac{3}{2}R,\ c_p = \frac{5}{2}R$

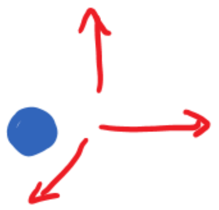
Diatomic gas: $c_V = \frac{5}{2}R,\ c_p = \frac{7}{2}R$

Monatomic vs diatomic gas

Monatomic gas: $c_V = \frac{3}{2}R,\ c_p = \frac{5}{2}R$

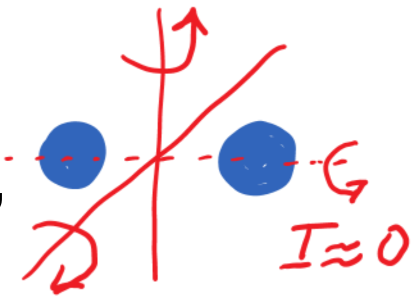
Diatomic gas: $c_V = \frac{5}{2}R,\ c_p = \frac{7}{2}R$

Each degree of freedom in the kinetic energy contributes $\frac{1}{2}R$ to specific heat

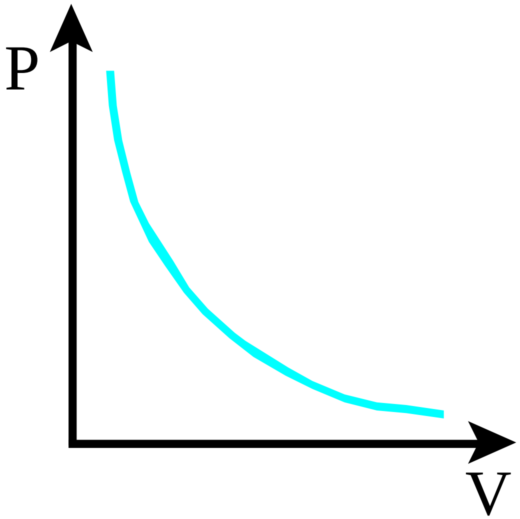


Monatomic gas: 3 directions for translation

Diatomic gas: 3 translations, 3 rotations,
but very small moment of inertia about one axis,
this rotation does not contribute



Adiabatic Process for ideal gas



$$Q = 0 \;\rightarrow \Delta U = -W$$

$$dU = -pdV$$

$$nc_V dT = -\frac{nRT}{V}dV$$

$$c_V ln\frac{T}{T_0} = -Rln\frac{V}{V_0}$$

$$\frac{T}{T_0} = \left(\frac{V}{V_0}\right)^{-\frac{R}{c_v}} = \left(\frac{V}{V_0}\right)^{1-\gamma}$$

$$c_p - c_V = R$$

$$\gamma = \frac{c_p}{c_v}$$

$\gamma = 1.67\ monatomic$

$\gamma = \ 1.40\ diatomic$

$$TV^{\gamma-1} = constant$$

$$pV^{\gamma} = constant$$