Objectives

# Ch 19 : The kinetic theory of gases

19.1 Avogadro's number

19.2 Ideal gases

19.3 Pressure, temperature, and RMS speed

19.4 Translational kinetic energy

~~19.5~~ ~~19.6~~

19.7 The molar specific heat of an ideal gas

~~19.8~~

19.9 Adiabatic expansion for an ideal gas.

Pressure

temperature

Internal energy

macroscopic properties of gases

Kinetic theory of gases

motion of molecules

# 19-1 Avogadro's number

$$N_A = 6.02 \times 10^{23} / \text{mole}$$

one mole contains Avogadro's number.

12 g of Carbon contains $6.02 \times 10^{23}$ atoms

$\Rightarrow$ 1 mole of carbon $\equiv$ 12 g.

number of moles

number of molecules

$$n = \frac{N}{N_A}$$

$N_A$ ← Avogadro's number.

mass of a sample

$$n = \frac{M_{sam}}{M}$$

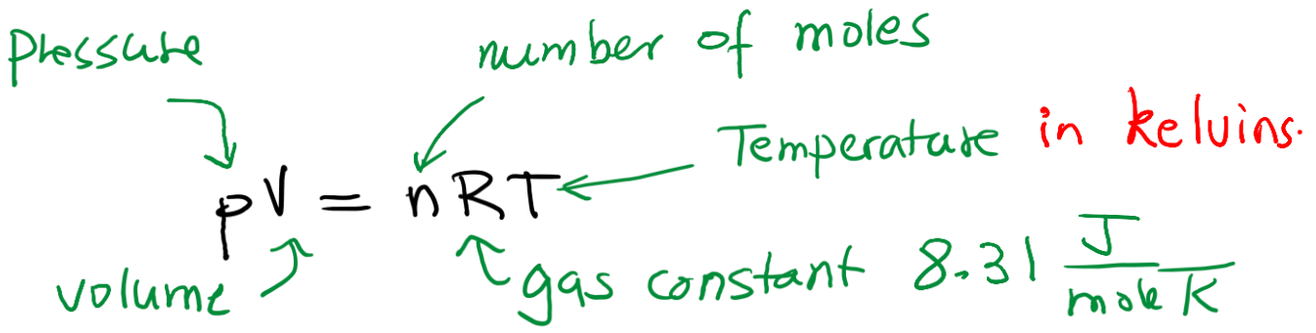
$M$: mass of one mole (molar mass)

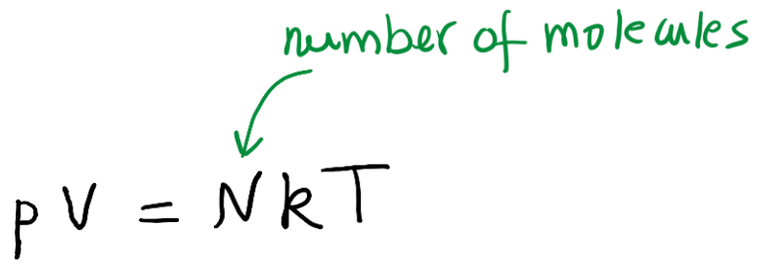
mass of one molecule (molecular mass)

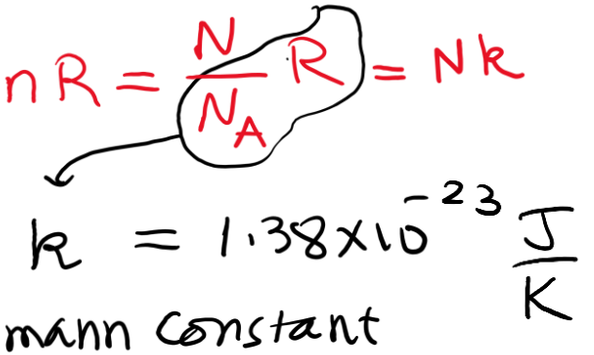
$$M = m N_A$$

# 19-2 Ideal gas law

At low densities, real gases tend to obey ideal gas law.



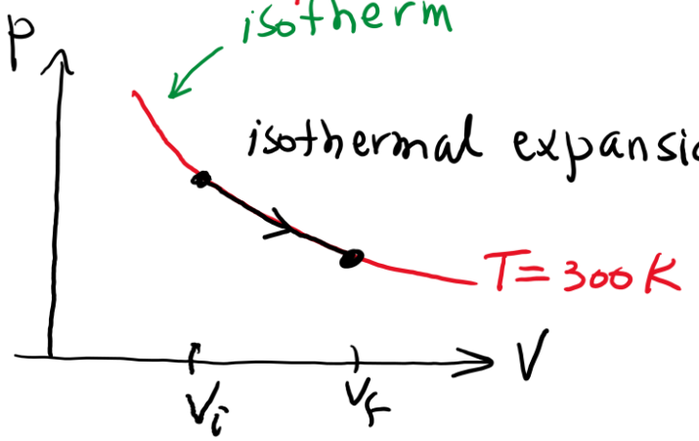



$$W = \int_{V_i}^{V_f} p\,dV$$

$$pV = nRT$$

## Isothermal process (same temperature)



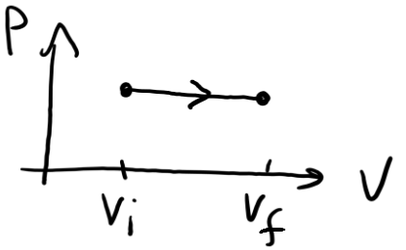

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{nRT}{V}\,dV$$

(nRT: constant)

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT\left[\ln V_f - \ln V_i\right]$$

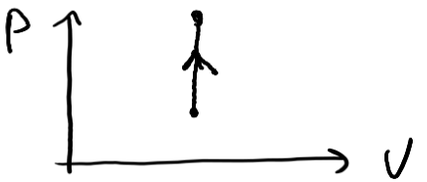
$$W = nRT \ln \frac{V_f}{V_i}$$

## Isobaric process (same pressure)




$$W = \int_{V_i}^{V_f} p\,dV = p(V_f - V_i)$$

## Isochoric process (same volume)




$$W = 0$$

Example

Oxygen (ideal)

$P_i = 15$ Atm
$V_i = 12$ L
$T_i = 27^\circ C$

$\Longrightarrow$

$P_f = ?$
$V_f = 6$ L
$T_f = 47^\circ C$

must be in kelvins

$$\left.\begin{aligned} P_i V_i &= nRT_i \\ P_f V_f &= nRT_f \end{aligned}\right\} \quad \frac{P_f V_f}{P_i V_i} = \frac{T_f}{T_i} \Rightarrow P_f = P_i \frac{V_i}{V_f} \cdot \frac{T_f}{T_i}$$

$$P_f = 15 \frac{12}{6} \frac{273+47}{273+27} = 32 \text{ Atm}$$

# 19-3 Pressure, Temperature, and RMS speed

Average kinetic energy per molecule

$$K_{avg} = \frac{\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \cdots + \frac{1}{2}mv_N^2}{N}$$

$$K_{avg} = \frac{1}{2}m\left[\sqrt{\frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N}}\right]^2$$

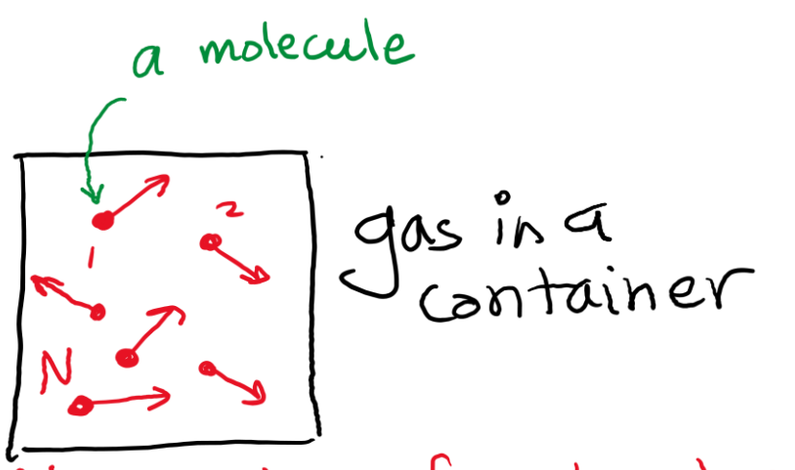
root-mean-square speed

$$K_{avg} = \frac{1}{2}m v_{rms}^2$$

$$v_{rms} \equiv \sqrt{\frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N}}$$

$$K_{avg} = \frac{1}{2}m\,\frac{3kT}{m} = \frac{3}{2}kT$$

$$\boxed{K_{avg} = \frac{3}{2}kT}$$




$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad (Nk = nR) \quad \sqrt{\frac{3nRT}{mN}}$$

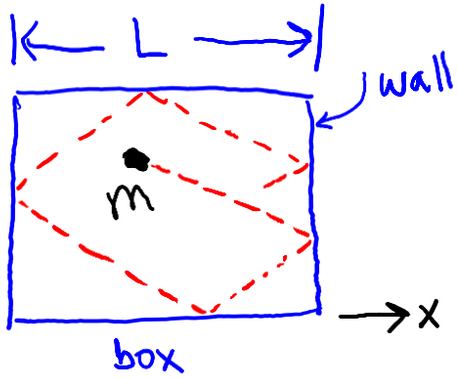
$\frac{3kT}{m}$: mass of one molecule

$$\frac{n}{mN} = \frac{1}{M} \qquad \sqrt{\frac{3RT}{M}}$$

$M$: molar mass

| | $v_{rms}$ |
|---|---|
| $H_2$ | 2000 |
| $N_2$ | 500 |

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$




Change in momentum
- molecule: $\Delta p_x = (-mv_x) - (mv_x) = -2mv_x$
- wall: $\Delta p_x = +2mv_x$

time between two collisions with the wall $\Delta t = \frac{2L}{v_x}$

Rate at which momentum is delivered to the wall $= \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{\frac{2L}{v_x}} = \frac{mv_x^2}{L} = F$

$$\Rightarrow \text{pressure } p = \frac{F}{A} = \frac{\frac{mv_x^2}{L}}{L^2} = \frac{mv_x^2}{L^3} = \frac{mv_x^2}{V}$$

N molecules

$$p = \frac{m}{V}\frac{(v_{x1}^2 + v_{x2}^2 + \cdots v_{xN}^2)}{N} N = \frac{mN}{V}(v_x^2)_{avg} = \frac{mN}{V}\frac{(v^2)_{avg}}{3}$$

$v_{rms}^2$

$$pV = \frac{mNv_{rms}^2}{3} = NRT \Rightarrow \boxed{v_{rms} = \sqrt{\frac{3RT}{m}}}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$(v_x^2)_{avg} = (v_y^2)_{avg} = (v_z^2)_{avg}$$

$$(v_x^2)_{avg} = \frac{(v^2)_{avg}}{3}$$

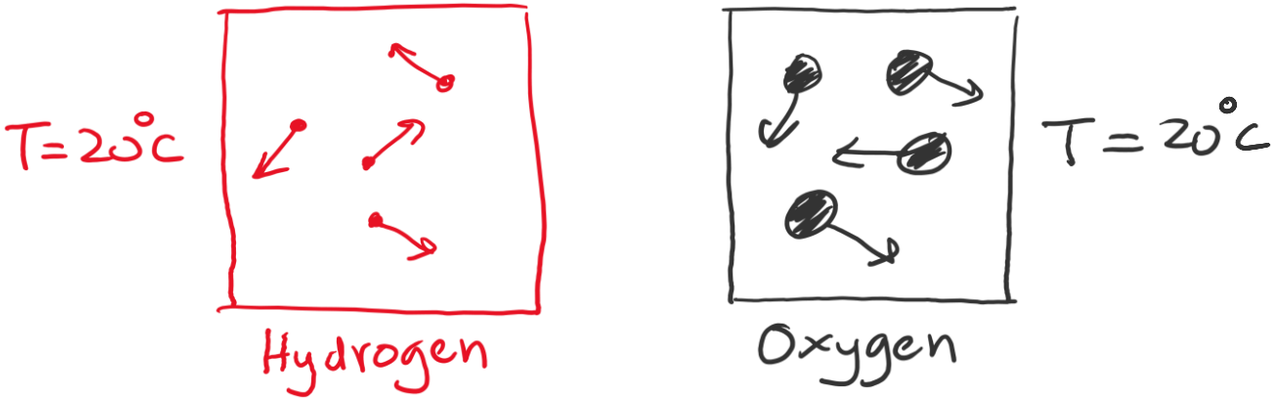
# 19-4 Translational Kinetic energy

Average Kinetic energy of <u>one</u> molecule

$$K_{avg} = \frac{3}{2} kT$$

↑ Boltzmann constant $1.38 \times 10^{-23} \frac{J}{K}$

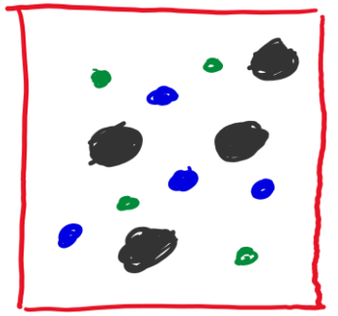
does not depend on mass.




$K_{avg}$ = $K_{avg}$

## Question

A gas mixture with three types of molecules



$m_1 > m_2 > m_3$

Compare:

Average kinetic energy

$$K_{avg_1} = K_{avg_2} = K_{avg_3}$$

Root mean square speed

$$v_{rms_1} < v_{rms_2} < v_{rms_3}$$

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

For a monatomic gas (made of individual atoms),

Internal energy ≡ Sum of translational kinetic energies of the atoms

$$E_{int} = N K_{avg} = N\left(\frac{3}{2}kT\right) = \frac{3}{2}nRT$$

$$E_{int} = \frac{3}{2}nRT$$

gas constant 8.31 J/mol.K

number of mdes

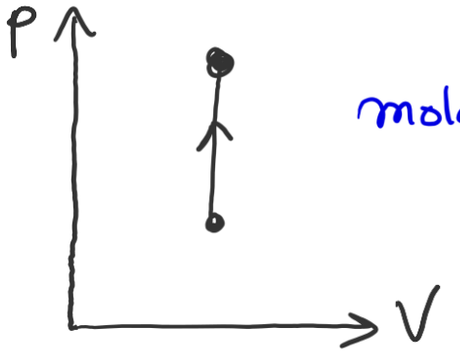
For a confined gas, $E_{int}$ depends only on the temperature.

# 19-7 The molar specific heat of an ideal gas

For solids or liquids $Q = mc\Delta T$ (c: specific heat)

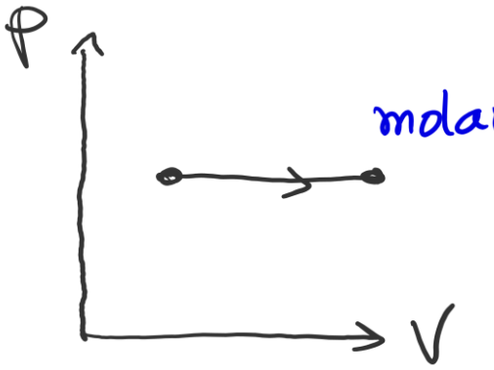
For gases $Q = nC\Delta T$ (C: heat capacity; C: molar specific heat)

But heat depends on path $\Rightarrow$ specify the path.




molar specific heat at constant volume

$C_V$

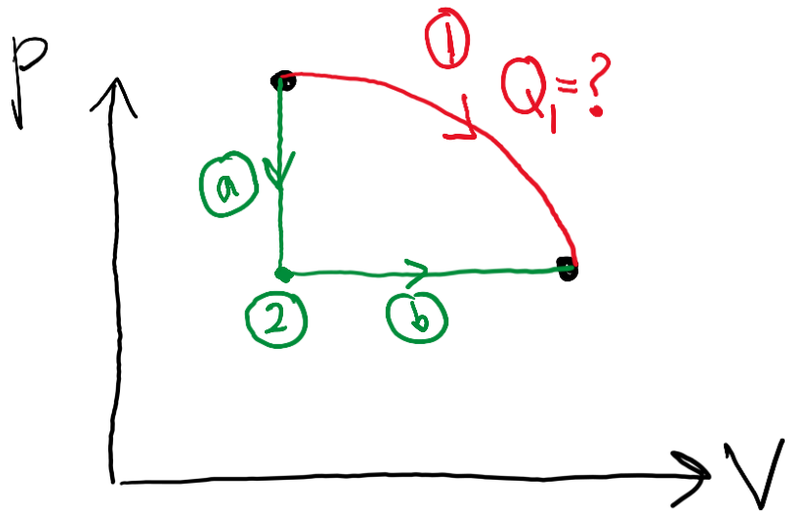



molar specific heat at constant pressure

$C_p$

For solids and liquids

$C_V \approx C_p = C$




$$\Delta E_{int,1} = \Delta E_{int,2}$$

$$Q_1 - W_1 = Q_2 - W_2$$

$$Q_1 = W_1 + Q_2 - W_2$$

area under the path

$$Q_2 = Q_a + Q_b$$

$nC_v\Delta T_a$ $\quad$ $nC_p\Delta T_b$

$\frac{C_v}{R}\Delta p_a V_a$ $\quad$ $\frac{C_p}{R} p_b \Delta V_b$

$$pV = nRT$$

(a) constant volume $\Rightarrow$ $\Delta p_a V_a = nR\Delta T_a$

(b) constant pressure $\Rightarrow$ $P_b \Delta V_b = nR\Delta T_b$

monatomic gas $E_{int} = \frac{3}{2} nRT$

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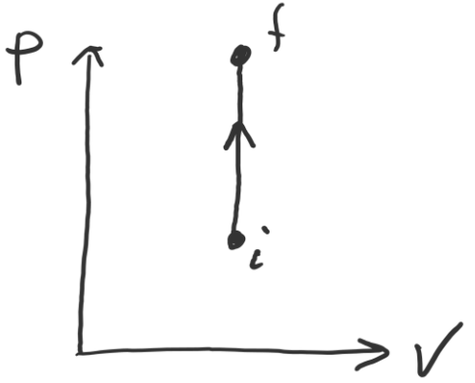


$\Delta E_{int} = Q - W$ ($W \to 0$)

$C_V$

$\frac{3}{2} nR\Delta T = Q$

$C_V = \frac{3}{2} R$

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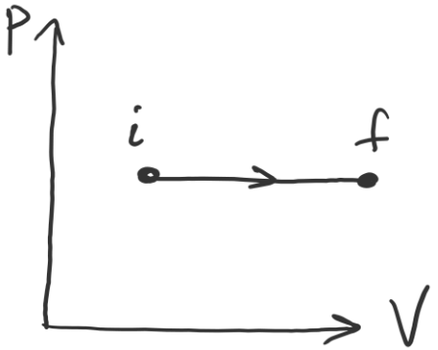


$\Delta E_{int} = Q - W$, $W = P\Delta V$

$pV = nRT \Rightarrow P\Delta V = nR\Delta T$

$\frac{3}{2} nR\Delta T = Q - nR\Delta T$

$C_P$

$\frac{5}{2} nR\Delta T = Q$

$C_P = \frac{5}{2} R$

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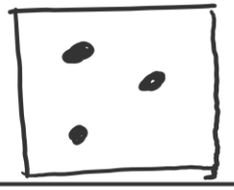
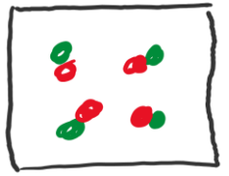
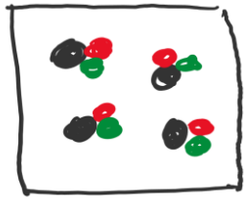
For any type of gas $C_P = C_V + R$

| Type of gas | $C_V$ | $E_{int}$ | $C_P = C_V + R$ | |
|---|---|---|---|---|
| Monatomic<br>Ar, He  | $\frac{3}{2}R$ | $n(\frac{3}{2}R)T$ | $\frac{5}{2}R$ | One atom per molecule |
| Diatomic<br>$H_2$, $N_2$  | $\frac{5}{2}R$ | $n(\frac{5}{2}R)T$ | $\frac{7}{2}R$ | two atoms per molecule |
| Polyatomic<br>$H_2O$  | $\frac{6}{2}R$ | $n(\frac{6}{2}R)T$ | $\frac{8}{2}R$ | more than two atoms per molecule |

$E_{int} = nC_VT$ Does not depend on path

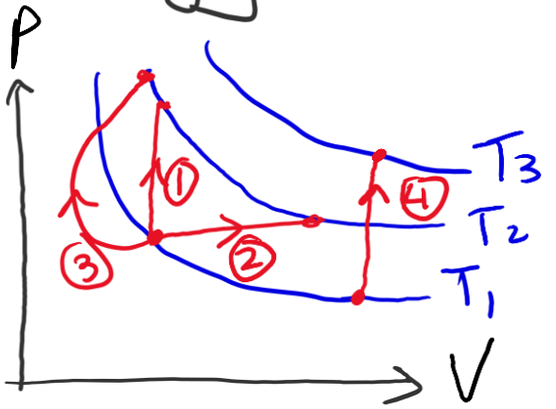
$C_V$ symbol ⇒ Nothing to do with constant volume

## Question

Compare change in internal energy

$$\Delta E_{int} = n C_v \Delta T$$

Does not depend on path

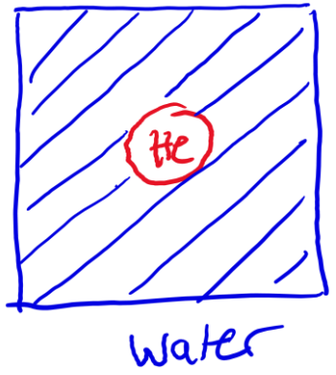



$$\Delta T_1 = \Delta T_2 = \Delta T_3 < \Delta T_4$$

$$① = ② = ③ < ④$$

# Example

A helium bubble in water

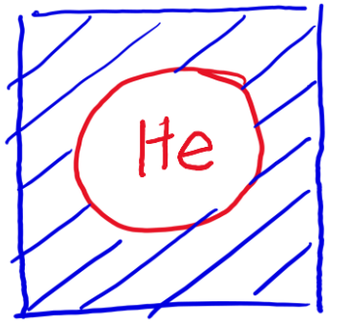



5 moles of helium (He)

Expansion

at the same pressure

$\Delta T = 20\ C^\circ$




Heat added to the bubble

$$Q = nC_p\Delta T = 5\left(\frac{5}{2}R\right)(20) = 2100\,J$$

Change in the internal energy of the bubble

$$\Delta E_{int} = nC_v\Delta T = 5\left(\frac{3}{2}R\right)(20) = 1300\,J$$

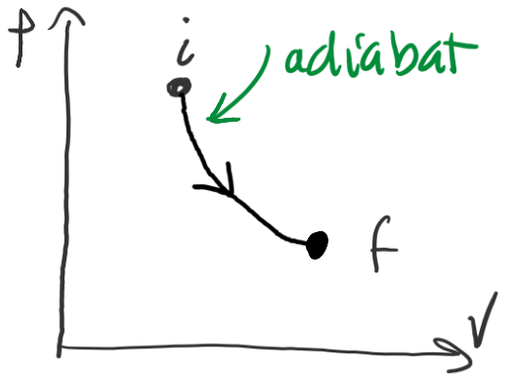
Work done by the bubble

$$\Delta E_{int} = Q - W \Rightarrow W = Q - \Delta E_{int} = 2100 - 1300 = 800\,J$$

# 19-9 The adiabatic Expansion of an ideal gas

An adiabatic process $\Rightarrow$ $Q = 0$

## reversible adiabatic process

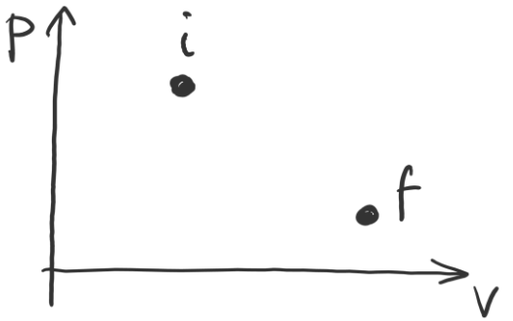



At any point between the initial and final state, the gas is close to equilibrium.

$\Rightarrow$ We know the pressure and volume

$\Rightarrow$ We can draw a path

## irreversible adiabatic process (Free expansion)




- process happens very fast
- We can not know pressure and volume

$\Rightarrow$ We cannot draw a path

# (Reversible) adiabatic expansion

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

$pV = nRT$

$\frac{nRT}{V} V^{\gamma} = \text{constant}$

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

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

$\gamma \equiv \frac{C_p}{C_v}$

monatomic $\gamma = \frac{5}{3}$

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

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

# Free expansion (Irreversible)

$pV = \text{constant}$ $\qquad P_i V_i = P_f V_f$

$pV = nRT \Rightarrow$

$T = \text{constant}$ $\qquad T_i = T_f$

## Example

One mole of oxygen expands adiabatically

| initial | final |
| --- | --- |
| $V_i = 12\,L$ | $V_f = 24\,L$ |
| $T_i = 300\,K$ | $T_f = ?!$ |

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1} = 300\left(\frac{12}{24}\right)^{\frac{7}{5}-1} = 227\,K$$

# Example

One mole of oxygen expands freely

| initial | final |
| --- | --- |
| $V_i = 12\ L$ | $V_f = 24\ L$ |
| $T_i = 300\ K$ | $T_f = ??$ |
| $P_i = 10\ Pa$ | $P_f = ??$ |

$$T_i = T_f = 300\ K$$

$$P_i V_i = P_f V_f$$

$$10(12) = P_f(24)$$

$$\Rightarrow P_f = 5\ Pa$$

Show that $TV^{\gamma-1} = \text{constat}$ for adiabatic expansion

$$\Delta E_{int} = \cancel{Q}^{0} - W$$

for small change

$$dE_{int} = -dW = -pdV$$

$$nC_V dT = -p\,dV \qquad pV = nRT$$

$$\cancel{n}C_V\,dT = -\frac{\cancel{n}RT}{V}dV$$

$$\int_{T_i}^{T_f}\frac{dT}{T} = \int_{V_i}^{V_f} -\frac{R}{C_V}\frac{dV}{V}$$

$$\Rightarrow \ln\frac{T_f}{T_i} = -\frac{R}{C_V}\ln\frac{V_f}{V_i} = \ln\left(\frac{V_i}{V_f}\right)^{\frac{R}{C_V}}$$

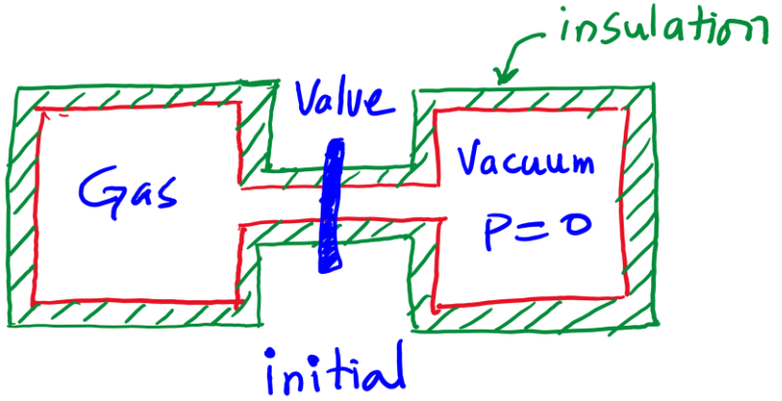
$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{\frac{R}{C_V}}$$

$$C_p = C_V + R$$

$$\frac{C_p - C_V}{C_V} = \frac{C_p}{C_V} - 1 = \gamma - 1$$

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

Show that $pV = \text{const}$ for free expansion




$Q = 0$

$W = 0$

$\Delta E_{int} = 0$

$$\Delta E_{int} = n C_v \Delta T = 0 \Rightarrow T_i = T_f$$

$$pV = nRT$$

$$\Delta(pV) = nR\Delta T = 0$$

$$\Rightarrow P_i V_i = P_f V_f$$