

# Recap from last time

n: number of moles

R: gas constant

(8.314 J mol<sup>-1</sup> K<sup>-1</sup>)

$$PV = nRT \text{ (for moles)}$$

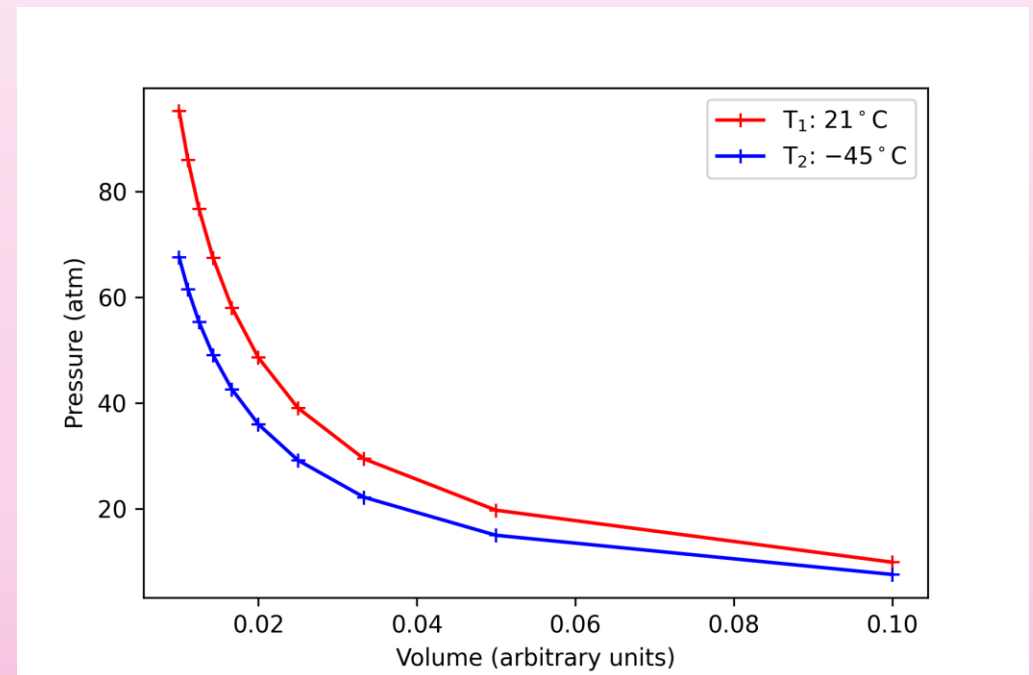
N: number of molecules =  $N_A \times n$

$k_B$ : Boltzmann's constant

( $1.38 \times 10^{-23}$  J K<sup>-1</sup>) =  $R/N_A$

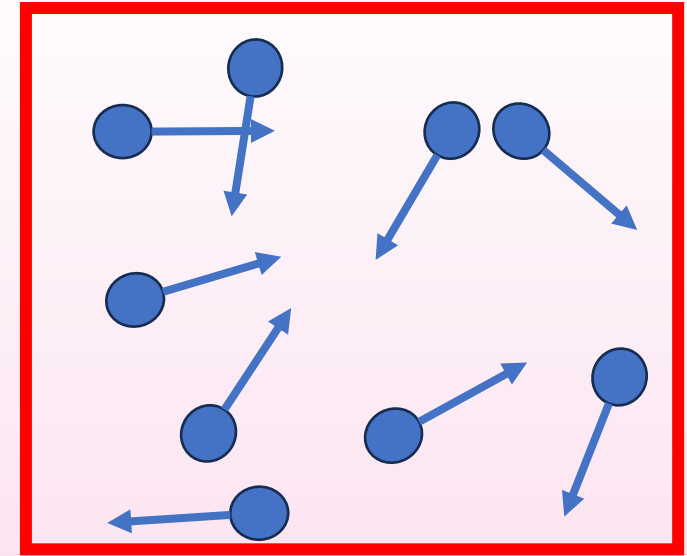
$$PV = Nk_B T \text{ (for molecules)}$$

An equation of state allows us to describe the macroscopic state of our gas – we usually do this on a **PV** diagram – a point on this plot represents a specific state

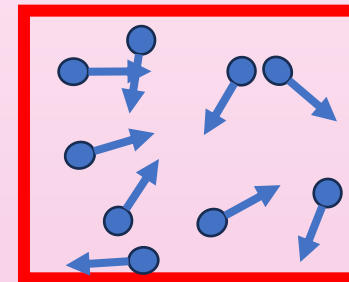


# Recap from last time

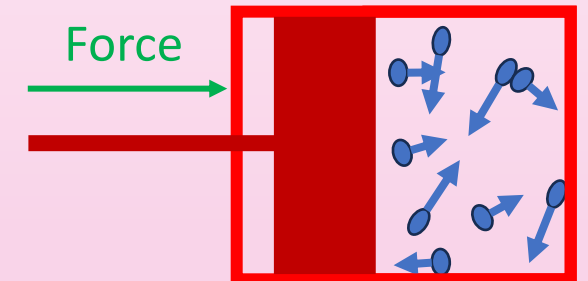
An ideal gas is a collection of molecules (or atoms, for a monatomic gas) that are non-interacting (no inter-atomic forces) that collide elastically



The internal energy of the gas is dependent on the velocities (kinetic energies) of the molecules, and hence on the temperature, and not on pressure and volume



1) Transfer heat to the gas



2) Do some work on the gas

# Recap from last time

From Joule's experiments (and logic), it is clear that the change in internal energy of a system,  $\Delta U$ , increases with increasing heat transferred into the system,  $Q_{in}$ , as well as work done on the system,  $W_{on}$

$$\Delta U = Q_{in} + W_{on}$$

We can also use this to define internal energy of a system...

Just an expression showing conservation of energy!

# Thermodynamic transitions

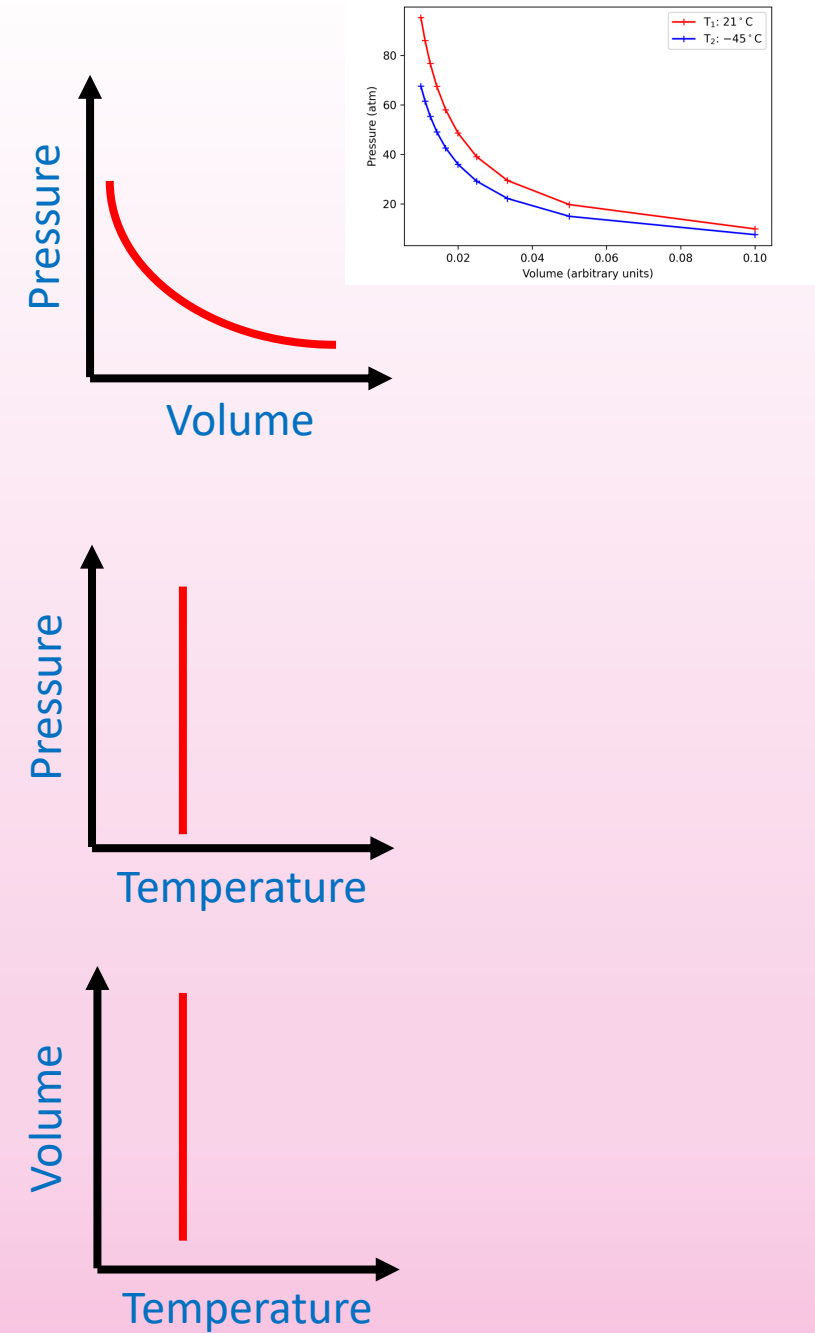
Isothermal (fixed temperature):

$$0 = Q_{in} + W_{on}$$

No change in temperature so  
no change in internal energy

$$\Delta T = \Delta U = 0$$

In PV plane,  $PV = \text{constant}$

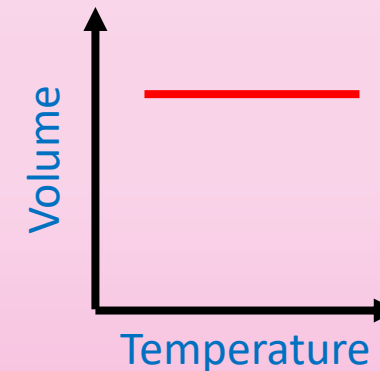
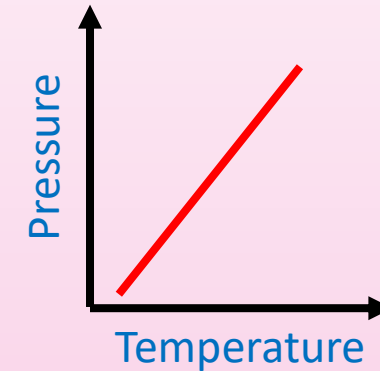
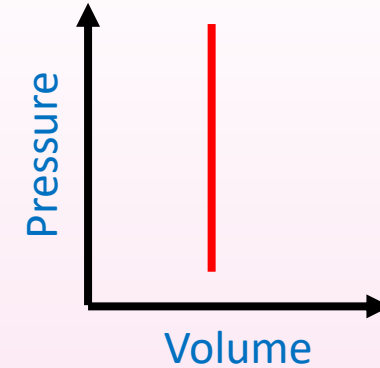


# Thermodynamic transitions

Isochoric (fixed volume):

$$\Delta U = Q_{in}$$

As  $W_{on} = (-) \int P dV$  and  $dV = 0$ ,  
 $W_{on} = 0$



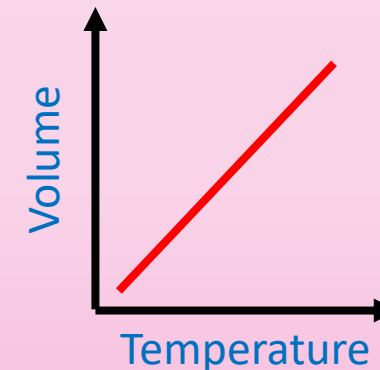
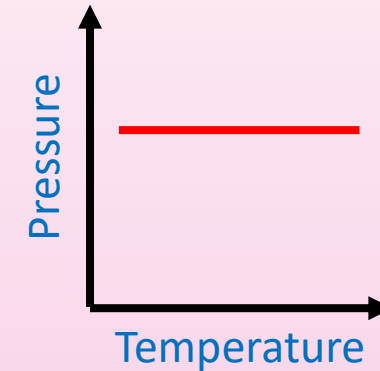
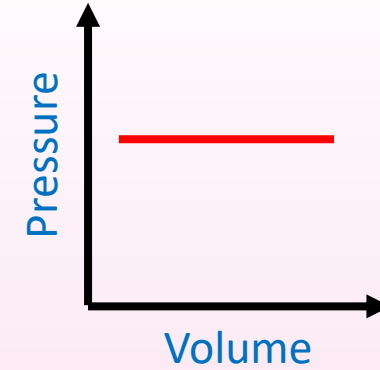
# Thermodynamic transitions

Isobaric (fixed pressure):

$$\Delta U = Q_{in} + P \Delta V$$

No non-zero terms here, but...

$$W_{on} = (-) \int P dV = (-)P \Delta V$$



# Heat capacities of (ideal) gases

Recall that  $\Delta Q = C\Delta T \rightarrow C = \frac{dQ}{dT}$  ... for gas, need more careful treatment

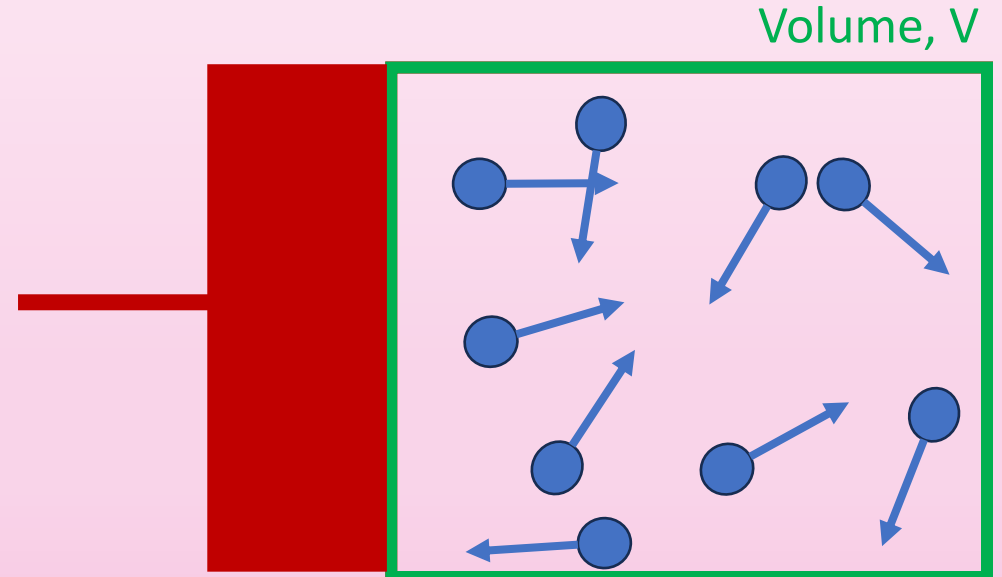
Molar heat capacity:  $C = nc$

At a constant volume:  $C_V = \left(\frac{dQ_{in}}{dT}\right)_V$

At a constant pressure:  $C_P = \left(\frac{dQ_{in}}{dT}\right)_P$

Mayer's relation:  $C_P = C_V + nR$

Thus it is clear that  $C_P < C_V$



# Molar heat capacity data (1 mole at 298 K)

Gas	$C_V$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_P$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_P - C_V$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Helium (He)	12.52	20.79	8.27
Argon (Ar)	12.45	20.79	8.34
Krypton (Kr)	12.45	20.79	8.34
Xenon (Xe)	12.52	20.79	8.27
Hydrogen (H <sub>2</sub> )	20.42	28.74	8.32
Nitrogen (N <sub>2</sub> )	20.76	29.07	8.31
Oxygen (O <sub>2</sub> )	20.85	29.16	8.31
Carbon monoxide (CO)	20.85	29.16	8.31

Remember that  $R = 8.31 \text{ J K}^{-1}$

Monatomic gases give  $C_P = 5R/2$ ,  $C_V = 3R/2$

Diatomic gases give  $C_P = 7R/2$ ,  $C_V = 5R/2$

Law of equipartition (much later... probably week 10)



# Thermodynamic transitions

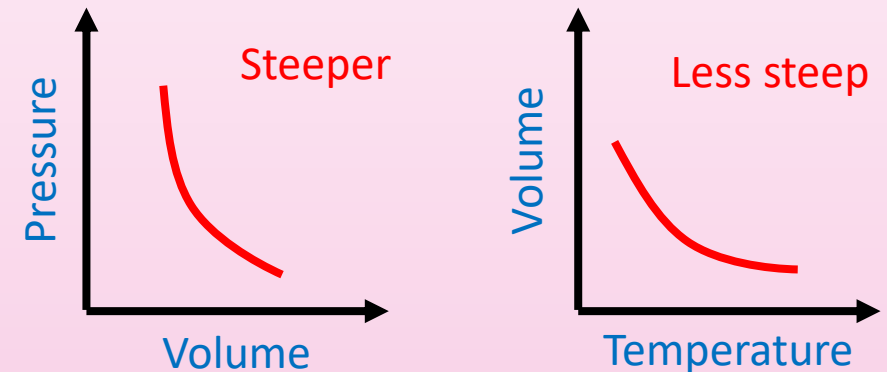
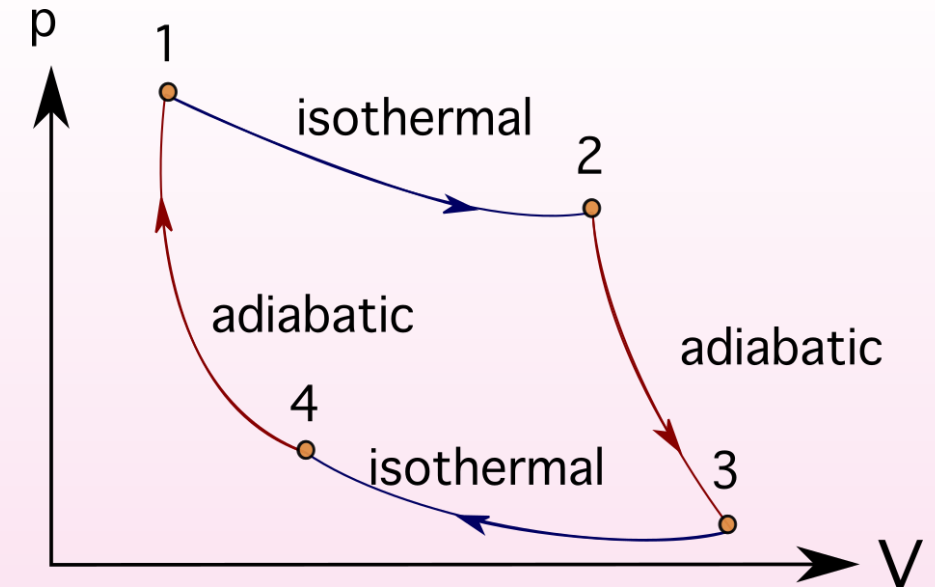
Adiabatic (no heat transfer):

$$\Delta U = W_{\text{on}}$$

No heat transfer, so  $Q_{\text{in}} = 0$

In PV plane, adiabatic processes are described by  $PV^\gamma = \text{constant}$

In VT plane, adiabatic processes are described by  $TV^{\gamma-1} = \text{constant}$



In the PV plane, adiabatic processes appear steeper than isothermal processes

Adiabatic processes are steeper in the PV plane than in the VT plane

# First law example question

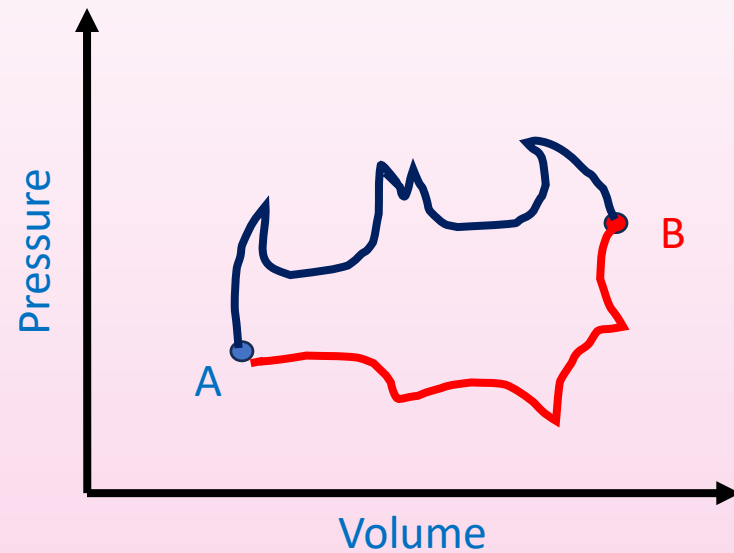
1 gram of water (volume =  $1 \text{ cm}^3$ ) is boiled at a fixed temperature and atmospheric pressure ( $1.01 \times 10^2 \text{ kPa}$ ) and turns into  $1671 \text{ cm}^3$  of steam.

The latent heat of vaporisation of water is  $2.26 \text{ MJ/kg}$

Calculate: i) the work done by the water/steam =  $167 \text{ J}$

ii) the change in internal energy of the water/steam =  $2093 \text{ J}$

# PV diagrams



We can move through the PV plane through processes, which usually involve some heat transfer and work (like in the case on the left)

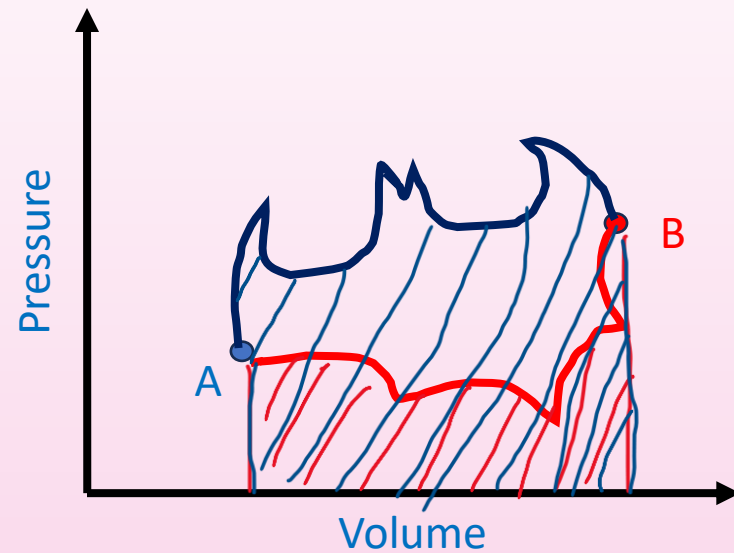
If we go along the blue path, is the change in internal energy  $U_{AB}$

- 1) Larger than if we went via the red path?
- 2) smaller than if we went via the red path?
- 3) The same as if we went via the red path?

As internal energy is a function of state it does not matter which path we take...

$U$  depends on solely on  $T$ , which itself depends on  $P$  and  $V$  (for same  $P$  and  $V$ , same  $T$  and hence same  $U$ )

# PV diagrams



$$W_{\text{blue}} > W_{\text{red}}$$

We can move through the PV plane through processes, which usually involve some heat transfer and work (like in the case on the left)

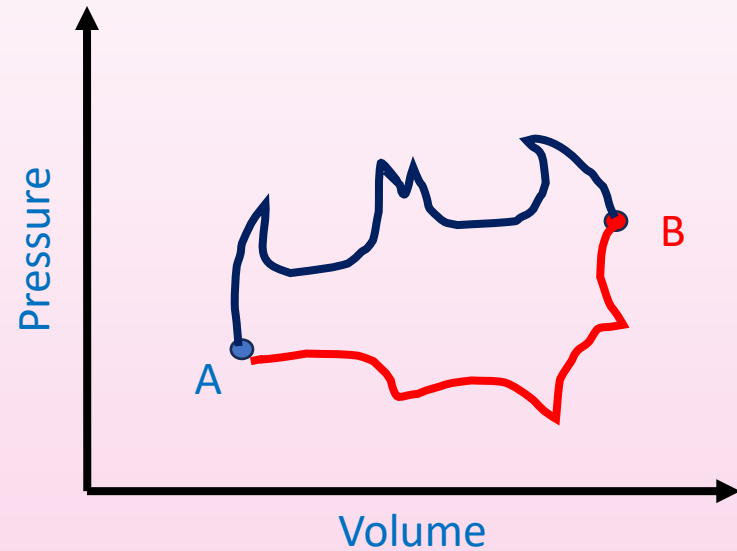
Is the work done by the gas,  $W_{\text{by}}$ ,

- 1) Greater for the red path?
- 2) Greater for the blue path?
- 3) The same for both paths?

$$W_{\text{by}} = \int P \, dV$$

Work is given by area under curve!

# PV diagrams



We can move through the PV plane through processes, which usually involve some heat transfer and work (like in the case on the left)

Is the heat input to the gas,  $Q_{in}$ ,

- 1) Greater for the red path?
- 2) Greater for the blue path?
- 3) The same for both paths?

$$\Delta U = Q_{\text{blue}} - W_{\text{blue}}$$

$$\Delta U = Q_{\text{red}} - W_{\text{red}}$$

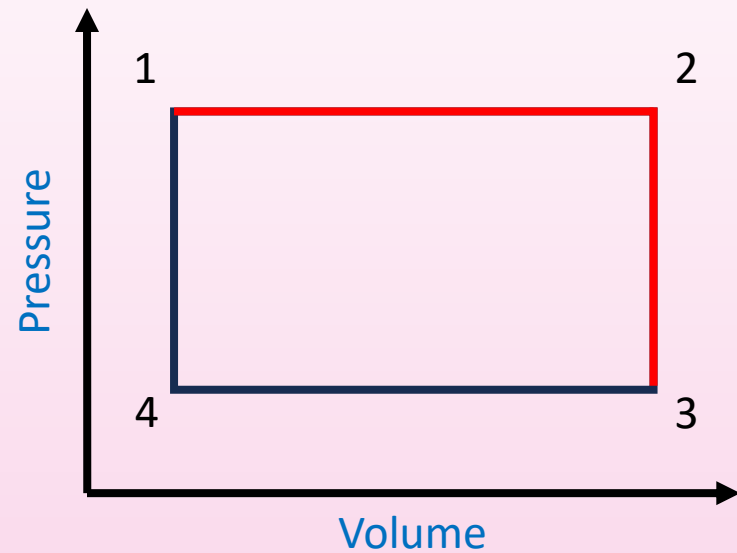
$$\Delta U = Q_{in} + W_{on} = Q_{in} - W_{by}$$

$$0 = Q_{\text{blue}} - W_{\text{blue}} - Q_{\text{red}} + W_{\text{red}}$$

$$W_{\text{blue}} > W_{\text{red}}$$

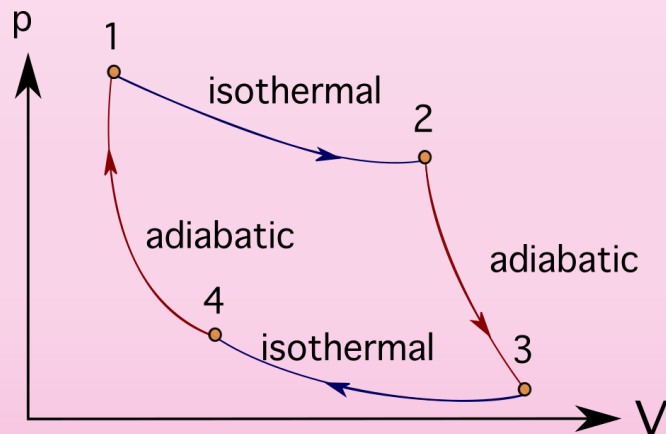
$$Q_{\text{blue}} > Q_{\text{red}}$$

# PV cycles



Rules for cycles:

- 1)  $\Delta U = 0$  for a full cycle ALWAYS
- 2) Work done given by area under PV plane (positive, which makes sense)
- 3)  $Q_{in}$  and  $W_{on}$  must sum to zero (as  $\Delta U = 0$ )



# Summary

Learnt how different thermodynamic processes look when viewed on the PV, VT and PT planes (PV most commonly used)

Learnt about the relationship between the molar heat capacity at constant volume ( $C_V$ ) and constant pressure ( $C_p$ ):  $C_p = C_V + nR$

Discussed how to determine relative heat, work and internal energy for different paths on a PV diagram, as well as an introduction to cycles