Thermal Physics

Lecture 5 – Work, P-V, Molar specific heats

Textbook reference: 18.4-18.6, 19.7-19.8

SpaceX:

https://youtu.be/A0FZIwabctw
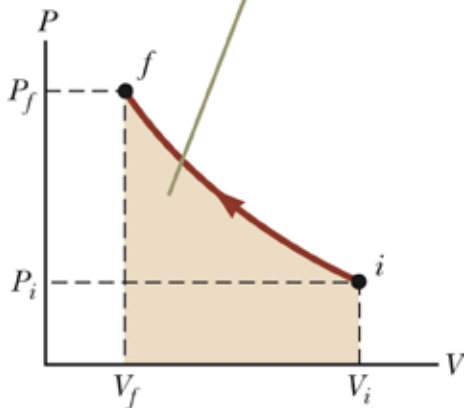https://youtu.be/bvim4rsNHkQ

Last Lecture

First Law of Thermodynamics $\Delta E_{int} = Q + W$

The work done on a gas equals the negative of the area under the *PV* curve. The area is negative here because the volume is decreasing, resulting in positive work.
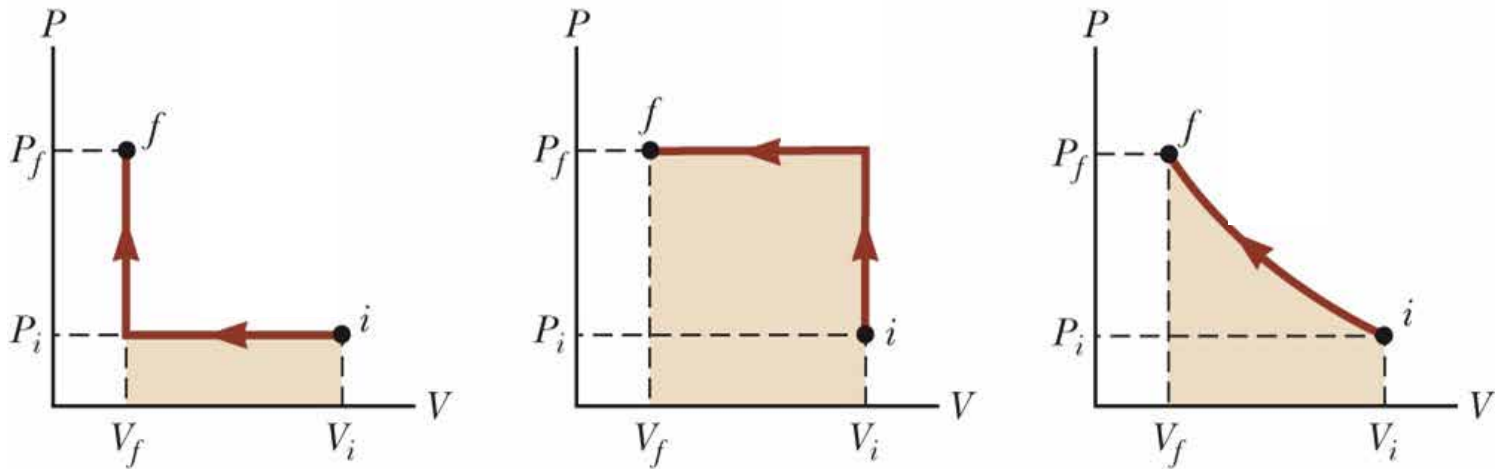
$$dW = -PdV$$

$$W = -\int_{V_i}^{V_f} PdV$$

Work done on a gas, W, is negative for expansions and positive for contractions.

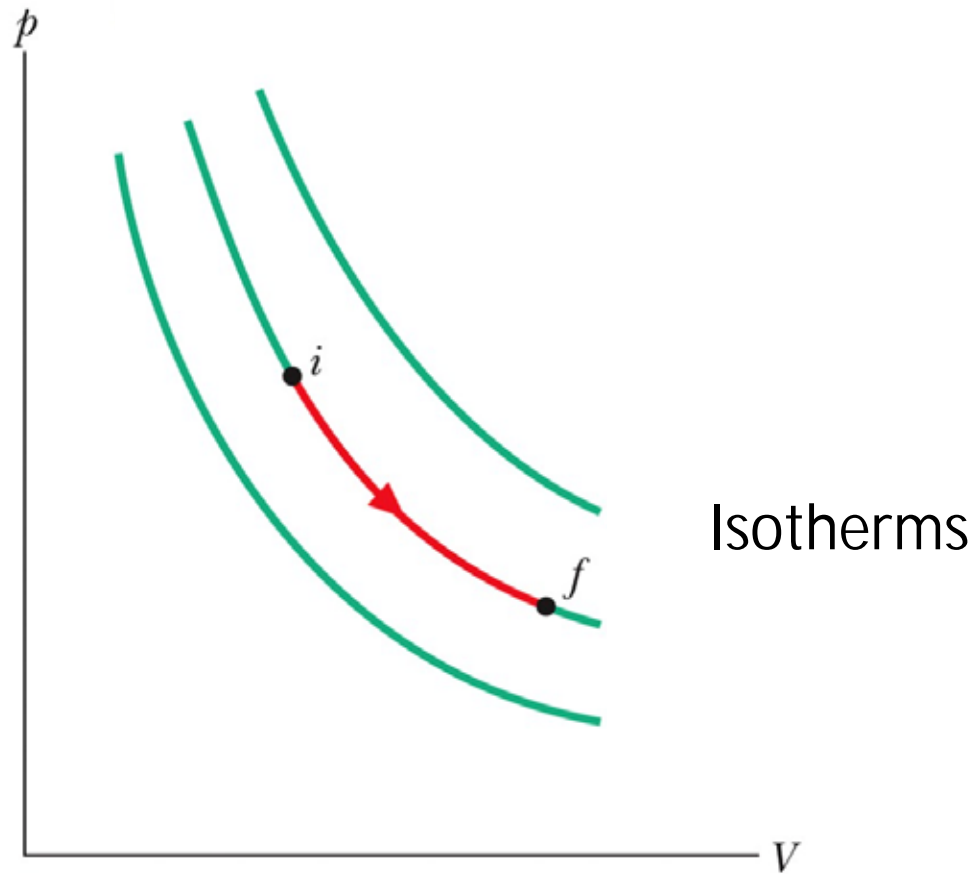When a gas expands the gas is doing the work.
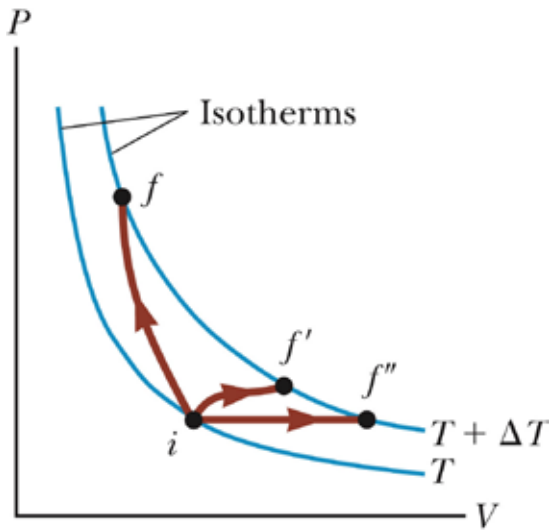
Last Lecture

The heat added to a system to get from state with V_i, P_i, T_i to a state with V_f, P_f, T_f changes, depending on the path (intermediate states)

PV plots

Isotherms

Molar specific heats

When we put heat into a gas, how hot does it get?

Gasses have a specific heat. We state molar specific heats for gasses, that is the amount of heat needed to raise one mole of a gas by 1 Kelvin.

We can write down a generic equation like this:

Heat required $\longrightarrow$

$$Q = nc_{\mathrm{molar}}\Delta T$$

$\longleftarrow$ (Final – initial) temperature

Number of moles of gas $\nearrow$

c_{molar} is a property of the type of gas under consideration. But there's a bit more to it...

But the molar gas constant isn't constant

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.
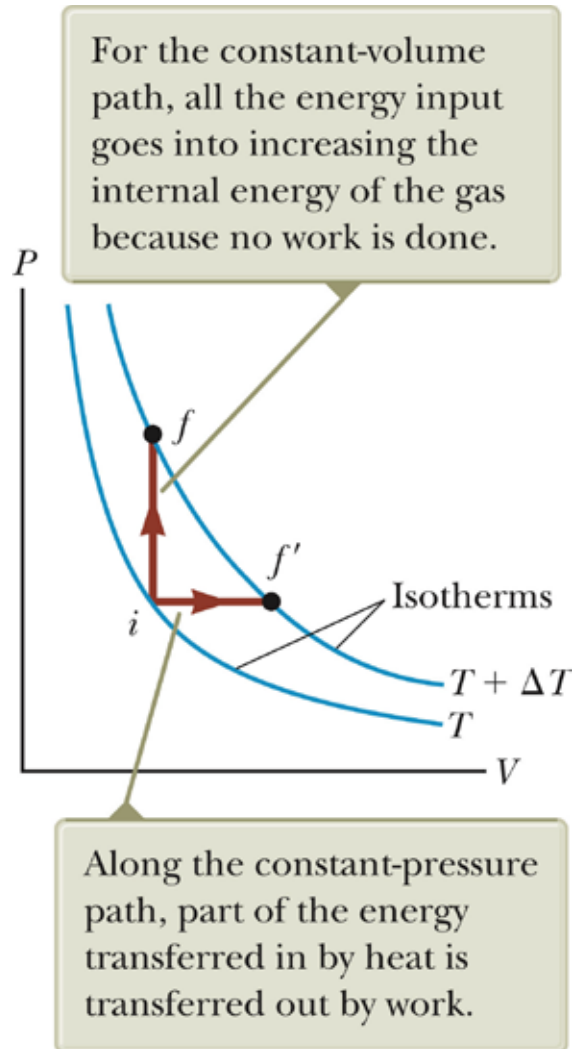
$$\Delta E_{int} = Q + W$$

$$E_{int} = \frac{3}{2} N k_B T$$

Monatomic ideal gas

$$\Rightarrow \Delta E_{int} = \frac{3}{2} N k_B \Delta T$$

If temperature changes a fixed amount the internal energy changes a fixed amount.

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

(Lines of constant temperature)

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

- The **molar specific heat** of gases is path-dependent.

$$\Delta E_{int} = Q + W$$

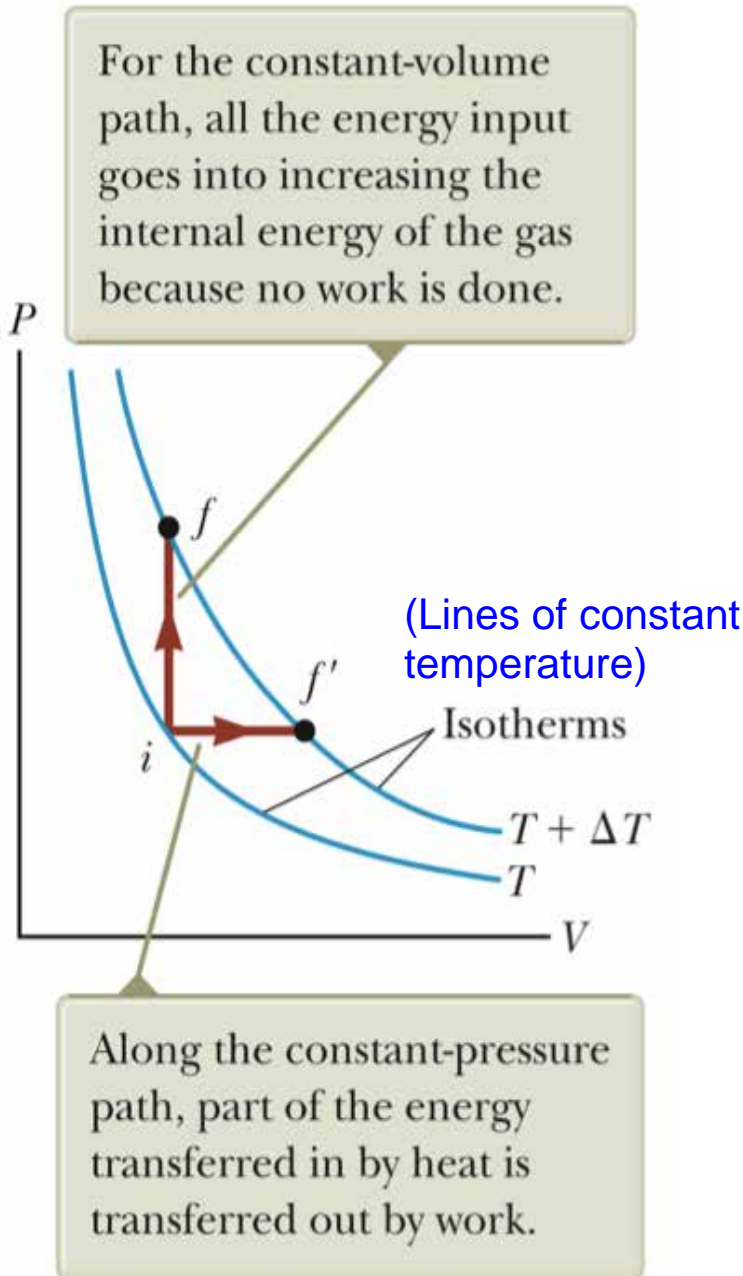- **Example**:

 – f and f' have the same internal energy.

 – Q needed to raise T by ΔT:
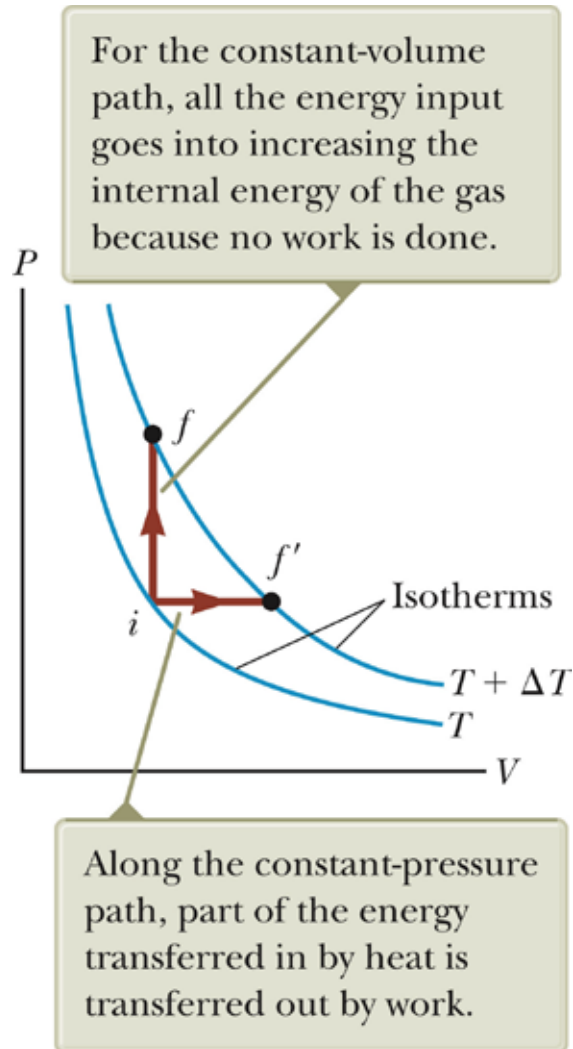
$$Q_{i \to f} = \Delta E_{int} = \frac{f}{2} nR\Delta T$$

$$Q_{i \to f'} = \Delta E_{int} - W_{i \to f'}$$
$$= \Delta E_{int} + |W_{i \to f'}|$$

Work is done by gas; $W < 0$

$i \to f'$ requires more heat than $i \to f$.

But the molar gas constant isn't constant

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

Isotherms

$T + \Delta T$

T

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.
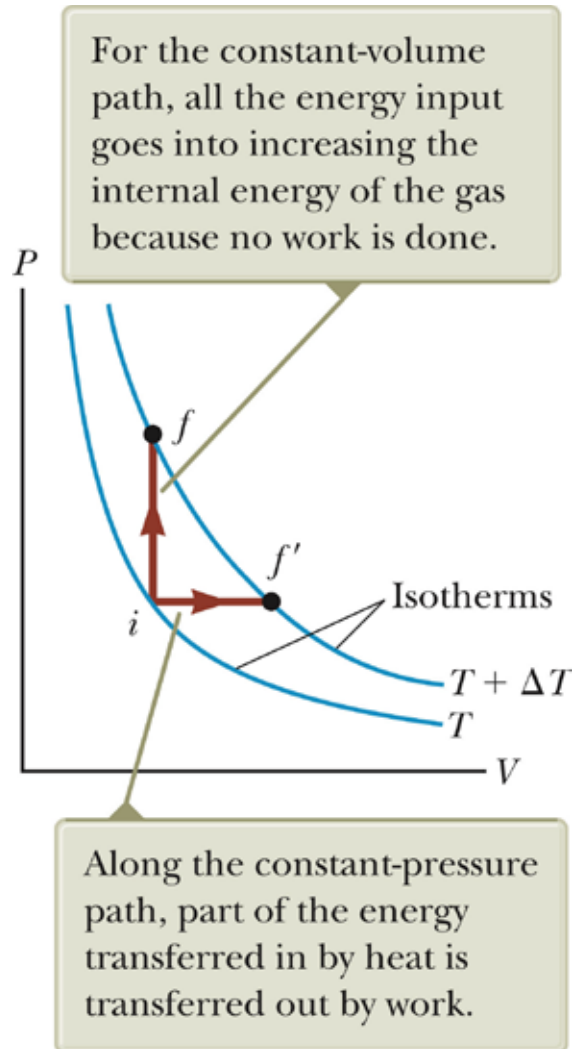
$$\Delta E_{int} = Q + W$$

As W is different for different paths, Q must be different for different paths as well.

$$Q = nC_{molar}\Delta T$$

But this can change

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

At constant volume

$$Q = nC_V \Delta T$$

Isotherms

$T + \Delta T$

T

At constant pressure

$$Q = nC_P \Delta T$$

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

Molar specific heat...

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

*Because of the path dependence, we define **two different molar specific heats**:
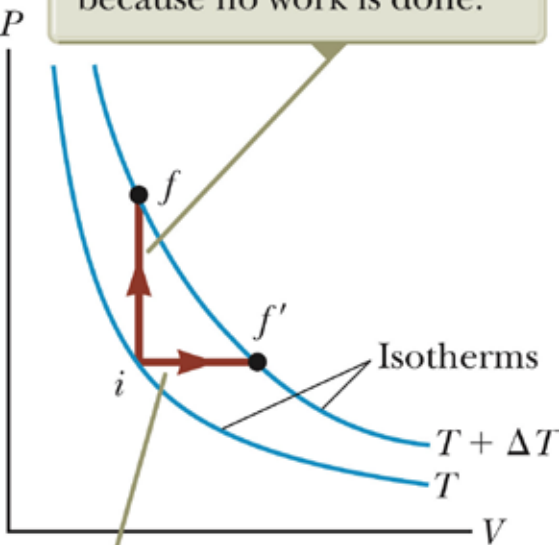
- Molar specific heat at constant volume c_V:

Heat required →

$$Q = nc_V\Delta T$$

← (Final – initial) temperature

↗ Number of moles of gas

- Molar specific heat at constant pressure c_P:

$$Q = nc_P\Delta T$$

P

f

f'

i

Isotherms

$T + \Delta T$

T

V

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.
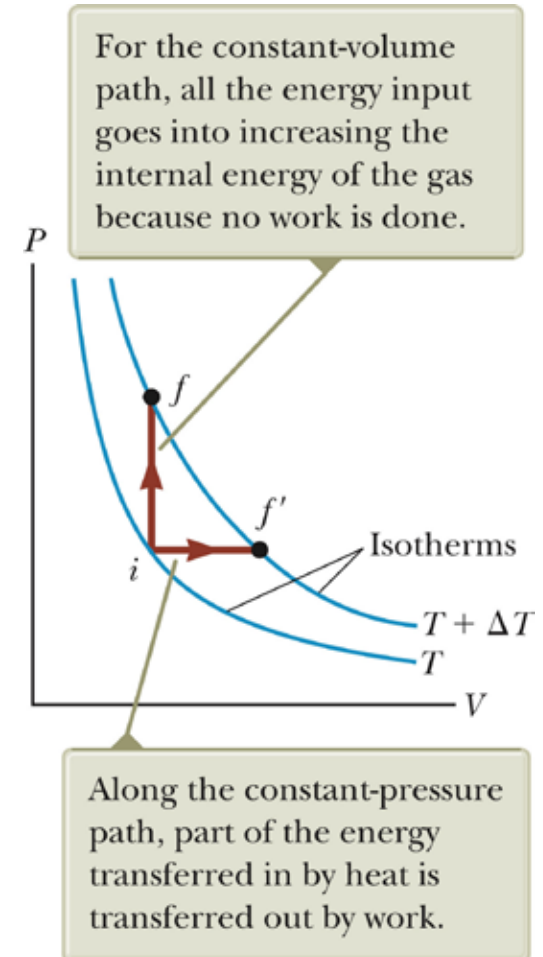
Question

Which is larger: C_V or C_P?

Hint:

$$\Delta E_{int} = Q + W$$

$$Q = nC_V \Delta T$$

$$Q = nC_P \Delta T$$

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

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

Isotherms

$T + \Delta T$
T

Molar specific heat: Constant volume...

Constant volume means no work is done on or by the gas.

– From the first law of thermodynamics:

$$\Delta E_{int} = Q$$

$$\Delta E_{int} = \frac{f}{2}nR\Delta T$$

$$Q = nc_V\Delta T$$

$$c_V = \frac{f}{2}R$$

Molar specific heat at constant volume

Universal gas constant

Gas molecules' number of degrees of freedom, e.g., f=3 for monatomic molecules

For a monatomic gas f=3: $C_V = 12.47 \ \mathrm{J/mol \cdot K}$

Table 21.1

Molar specific heats of various gases

Gas	Molar specific heat (J/mol.K)[a]			
	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Diatomic gases				
H_2	28.8	20.4	8.33	1.41
O_2	29.4	21.1	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic gases				
CO_2	37.0	28.5	8.50	1.30
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a] All values except that for water were obtained at 300 K.

The molar specific heat of hydrogen as a function of temperature.

The horizontal scale is logarithmic.

Hydrogen liquefies at 20 K.

Vibration

Rotation

Translation

$\frac{7}{2}R$

$\frac{5}{2}R$

$\frac{3}{2}R$

C_V (J/mol · K)

Temperature (K)
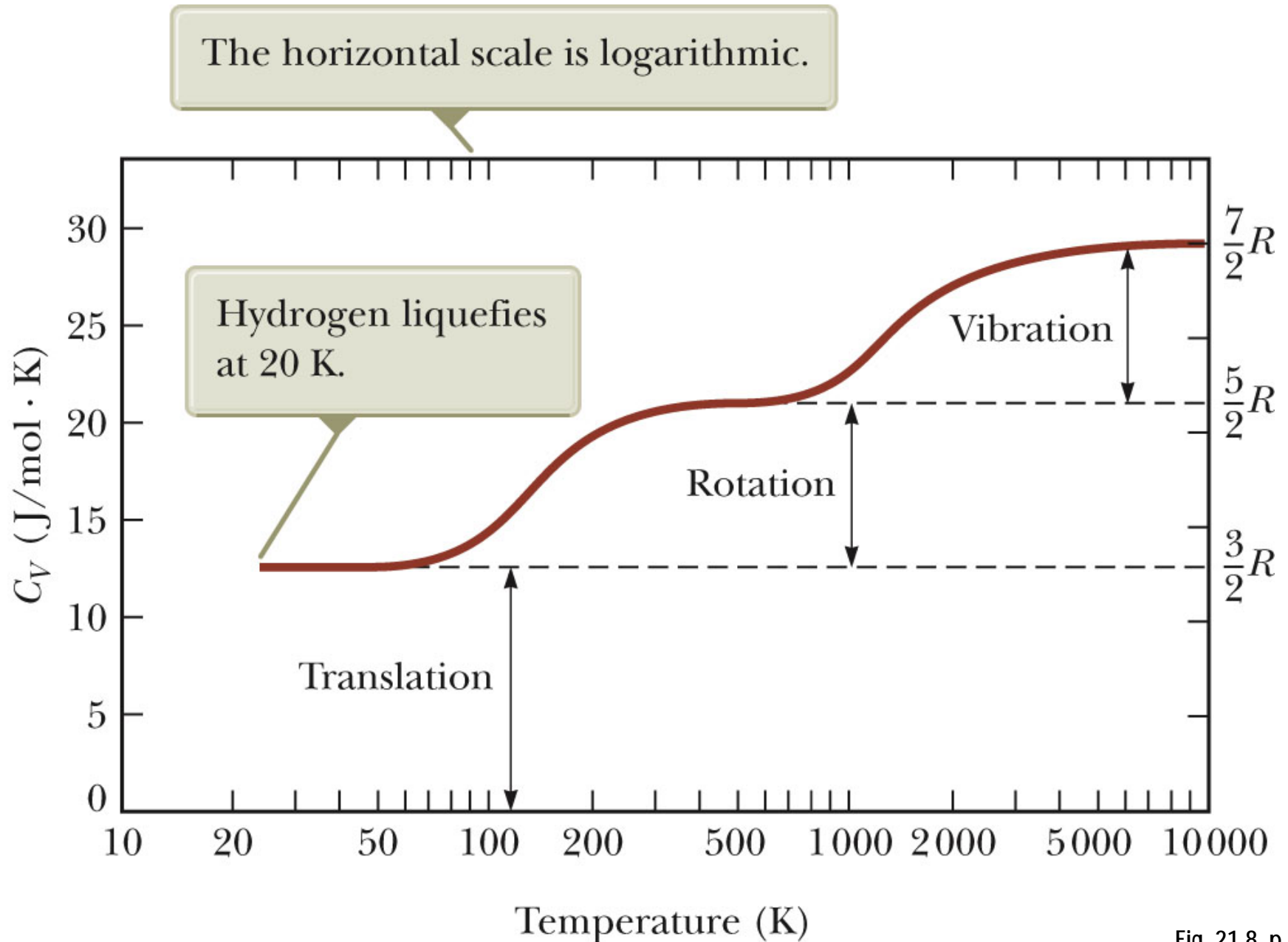
Molar specific heat:Constant pressure...

From the first law of thermodynamics:

$$\Delta E_{int} = Q + W$$

We can show that :   BLACKBOARD

$$c_P = \frac{f + 2}{2} R = c_V + R$$

$$C_P - C_V = R$$

Table 21.1

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[a] All values except that for water were obtained at 300 K.

γ diverges from 1.67 due to intermolecular interactions which we have ignored in the ideal gas assumption.

$$\gamma = \frac{C_V + R}{C_V}$$

$$c_V = \frac{f}{2} R$$

Ratio of specific Heats

$$\gamma = \frac{C_P}{C_V}$$

For monatomic gas:
$$\gamma = \frac{5/2R}{3/2R} = \frac{5}{3} = 1.67$$

We will meet γ again later.

Molar specific heats: Summary

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

$$C_P - C_V = R$$

$$C_P = \frac{f+2}{2}R$$

Adiabatic processes...

An adiabatic process is one in which no energy enters or leaves a system as heat.

$$Q = 0$$

- From the first law of thermodynamics, this means the only way you can change the internal energy of a system in a adiabatic process is to do work.

$$\Delta E_{int} = W$$

Adiabatic processes... $Q = 0$

- To minimise heat transfer, you can:

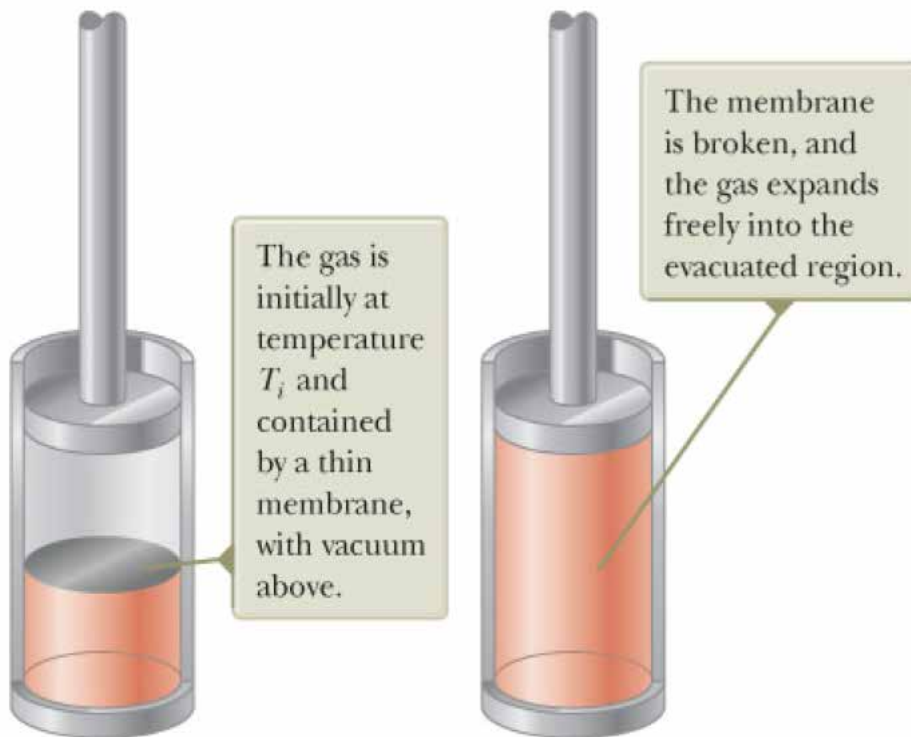 – **Insulate** the walls of the container very well.

  - Kind of obvious.

  – Perform the process **very quickly**.

- So that the gas reaches a new equilibrium state before there is time for heat to enter the system.
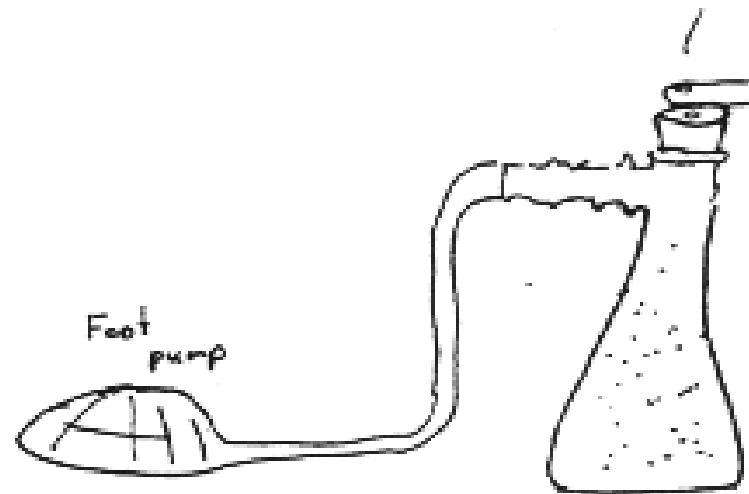
Adiabatic processes: **free** expansion...

No heat transfer into or out of the system.

The gas is initially at temperature T_i and contained by a thin membrane, with vacuum above.

The membrane is broken, and the gas expands freely into the evacuated region.

What can we say about the gas's temperature?

https://goo.gl/forms/QLz3m9Kyg9z5Bs2m2

Demo Unit Hb13: adiabatic expansion

Foot pump

Adiabatic Processes and Temperature

- If the gas is compressed adiabatically, W is positive so $\mathrm{D}E_{int}$ is positive and the temperature of the gas increases.

- This is why spacecraft have heat shields. NOT because of "friction with the air." The air cannot get out of the way fast enough **à** rapid compression and heating.

Adiabatic Processes and Temperature

- Since $Q = 0$, $\Delta E_{int} = Q + W = W$
- If the gas expands adiabatically, the temperature of the gas decreases.

0:44 / 2:58

Homework: Have a beer

- Pressure released when you open the bottle.
- This is an adiabatic expansion!
- Rapid cooling **à** vapor forms
- Disclaimer: If you are under 18, do not have a beer.
  Beer is bad, mmkay

Adiabatic expansion, but **non-free**...

Free expansion is a special case... In this course we are mainly concerned with adiabatic expansion and compression processes that **do displace** the piston.

- In these cases, **work is done**:

$$W \neq 0$$

$$\Delta E_{int} \propto \Delta T$$

$$\Rightarrow \Delta E_{int} = Q + W = W$$

Q = 0 in adiabatic processes

- Expansion $\rightarrow W < 0 \rightarrow$ Temperature of gas decreases.
- Compression $\rightarrow W > 0 \rightarrow$ Temperature of gas increases.

Adiabatic Processes and Temperature

•If the gas is compressed adiabatically, *W* is positive so DE_{int} is positive and the temperature of the gas increases.

•This is why spacecraft have heat shields. NOT because of "friction with the air." The air cannot get out of the way fast enough **à** rapid compression and heating.

Adiabatic Processes and Temperature

- Since $Q = 0$, $\Delta E_{int} = Q + W = W$
- If the gas expands adiabatically, the temperature of the gas decreases.

Homework: Have a beer

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Be_____mkay

Relationship between P and V in an adiabatic expansion

Adiabatic processes>P-V relation...

- During an adiabatic process, P, V, and T all change.

  – But how exactly? BLACKBOARD

- Useful info:

  – An adiabatic process satisfies:

Applies to the whole process from i to f $\longrightarrow$ $\Delta E_{int} = W$
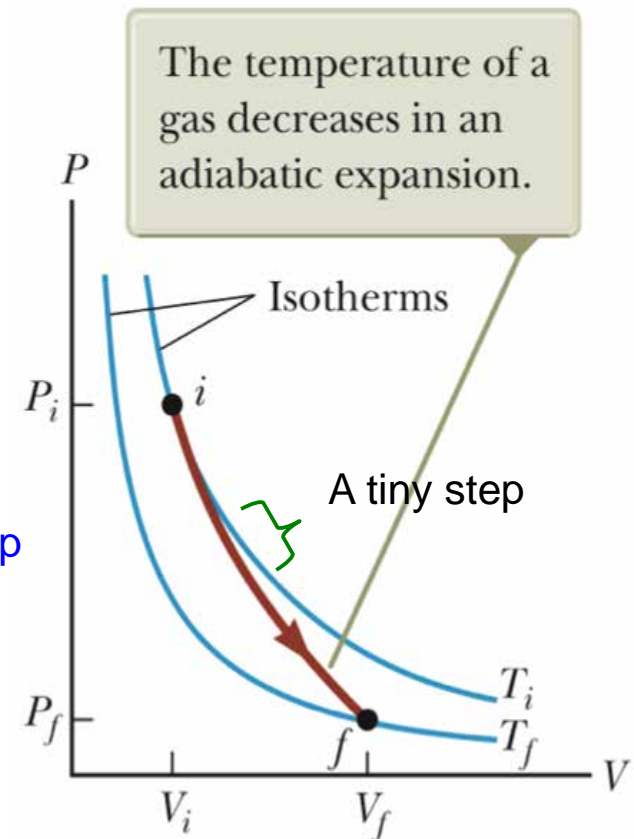
Or equivalently $dE_{int} = dW = -PdV$

What happens over a tiny step

  – We also know: $\Delta E_{int} = nC_V \Delta T$

$$dE_{int} = nc_V dT$$

$$\Rightarrow nc_V dT = -PdV$$

The temperature of a gas decreases in an adiabatic expansion.

Isotherms

P

P_i ──── i

A tiny step

P_f ──── f

T_i
T_f

V_i V_f V

Adiabatic processes>P-V relation...

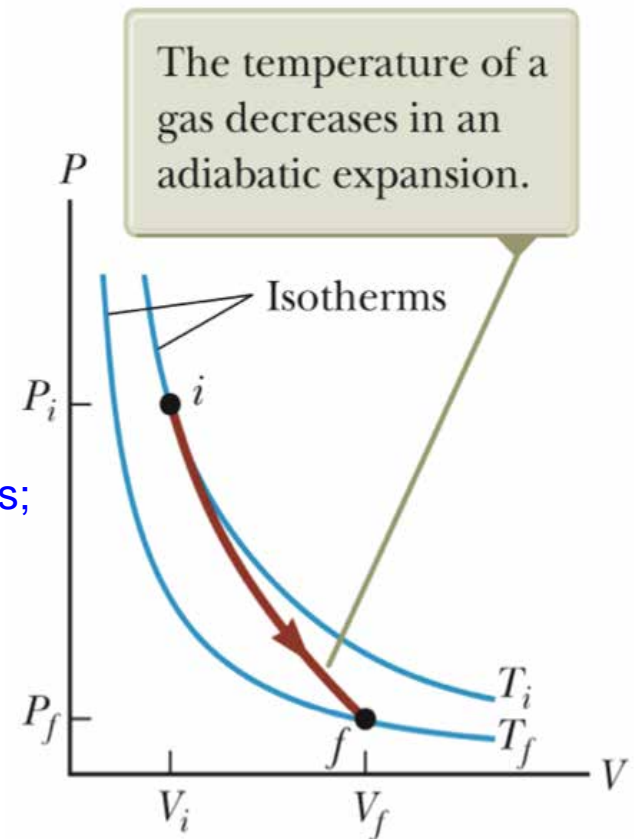- During an adiabatic process, P, V, and T all change.

- In an adiabatic process, pressure and volume are related by

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

Constant during the process; **not** a universal constant!
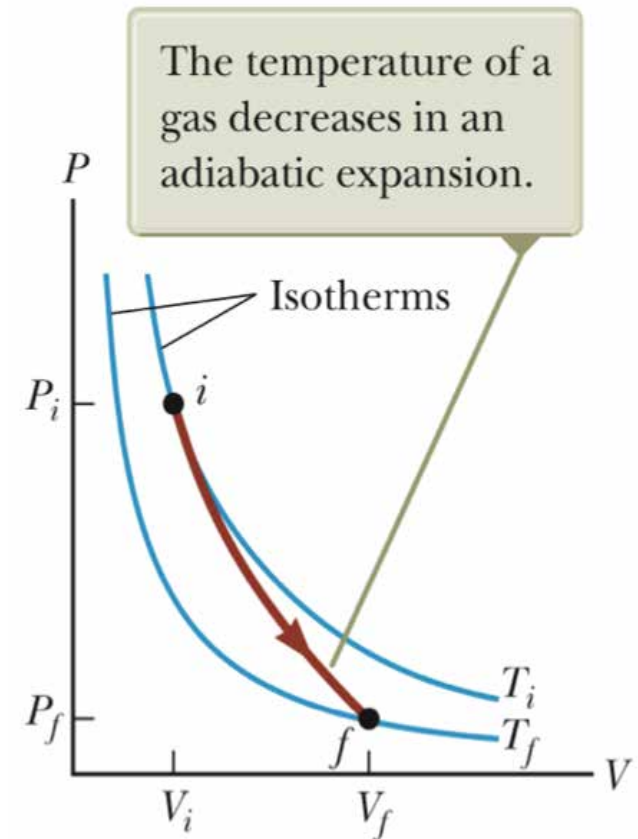
where

$$\gamma = \frac{c_P}{c_V}$$

The temperature of a gas decreases in an adiabatic expansion.

Adiabatic processes>T-V relation…

- There is a relation for temperature and volume too.

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

Constant during the process;
not a universal constant!

- Try to derive it yourself at home!

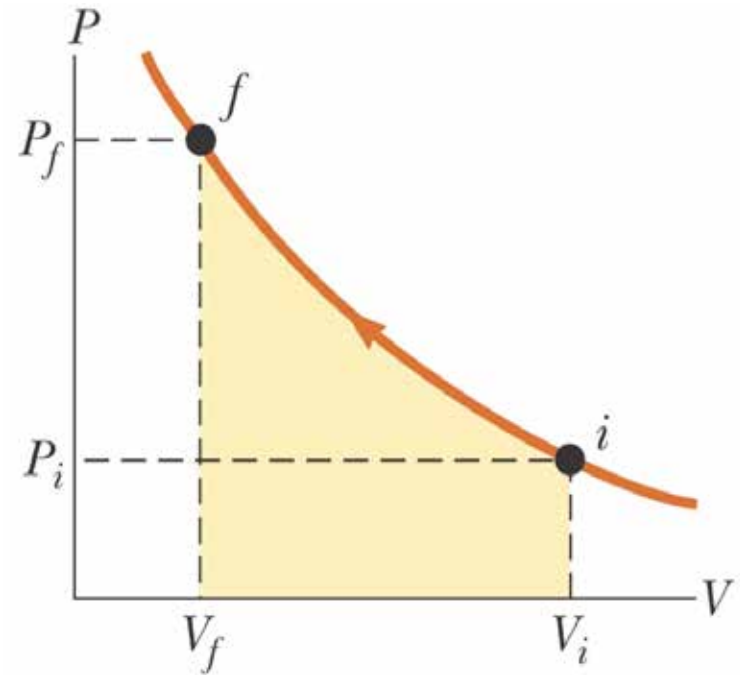The temperature of a gas decreases in an adiabatic expansion.

Isotherms

Named processes...

- There are literally an infinite number of possible paths connecting i and f on a PV-diagram...

A few of these paths even have names:

–Isothermal

–Isobaric

–Isovolumetric

–(Adiabatic, $Q = 0$)

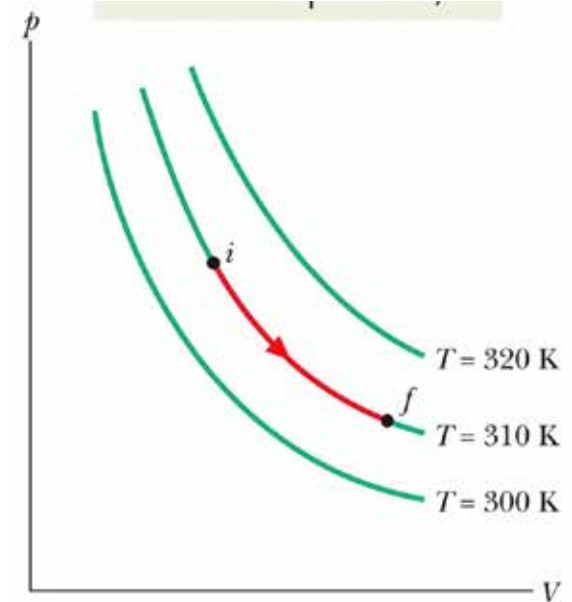© 2004 Thomson/Brooks Cole

Named processes: Isothermal...

An isothermal process is one carried out at **constant temperature**.

- For an isothermal process:

$$\Delta E_{int} = 0$$

$$PV = \text{constant}$$

p

i

f

$T = 320\ \text{K}$

$T = 310\ \text{K}$

$T = 300\ \text{K}$

V

- Any energy that enters the system by heat must leave the system by work.

Named processes: Isobaric…

A process carried out at **constant pressure**.

- – Work is generally nonzero because volume changes:

$$\frac{T}{V} = \text{constant}$$

- – Heat is also generally nonzero because temperature changes as work is done.

$$Q = nc_P\Delta T$$

Molar specific heat at constant pressure

Named processes>Isovolumetric...

A process that takes place at a **constant volume** is called an isovolumetric process.

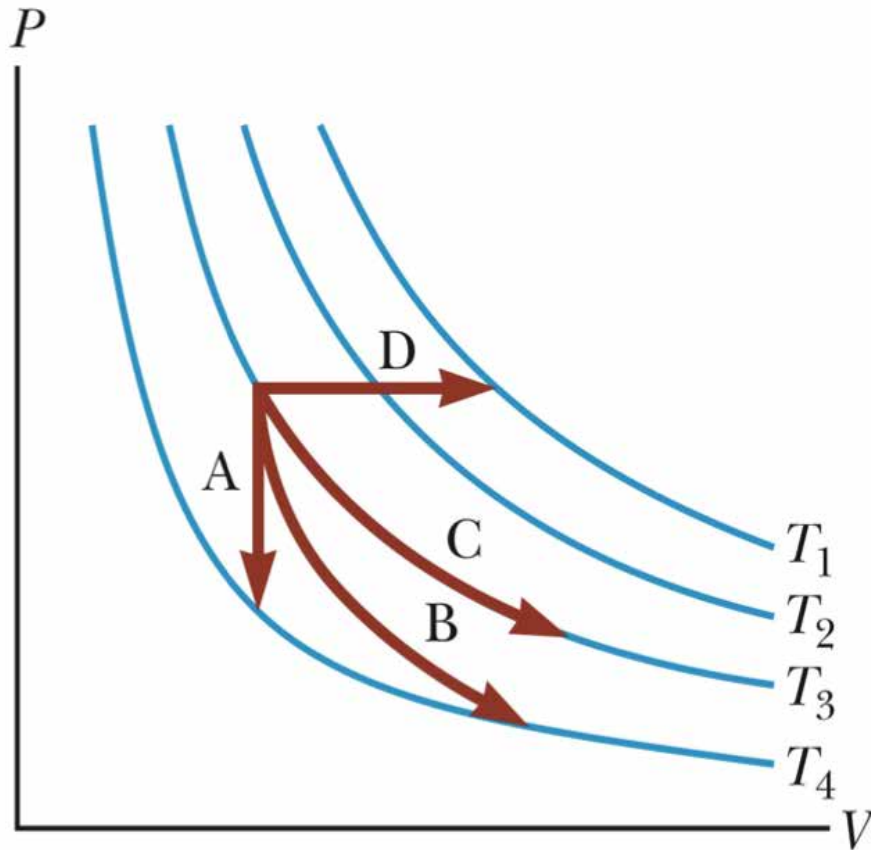- No work is done because the volume does not change.

$$W = \mathbf{0}$$

$$\Delta E_{int} = Q$$

Molar specific heat at constant volume

$$Q = nC_V \Delta T$$

Question...

- Name these 4 processes.

https://goo.gl/forms/QLz3m9Kyg9z5Bs2m2

Question

An ideal gas initially at 300 K undergoes an isobaric expansion at 2.50 kPa. If the volume increases from 1.00 m^3 to 3.00 m^3 and 12.5 kJ is transferred to the gas by heat, what are
a) the change in internal energy
b) its final temperature