

Specific heat - Cont.

Water: The Energy required to heat 1kg by 1K
is 4180 J/kg

A 50/50 water/antifreeze mix is about 3700 J/kg

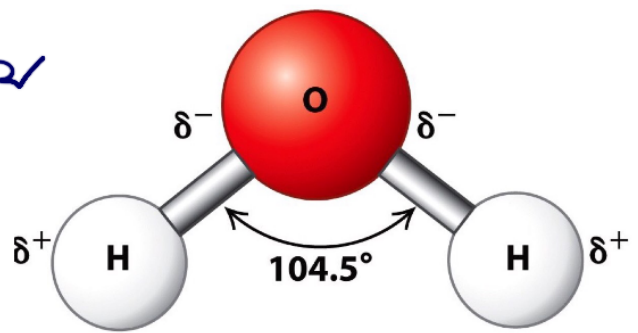
Energy stored per K. mol per degree of freedom.

$$= \frac{1}{2} R_u T$$

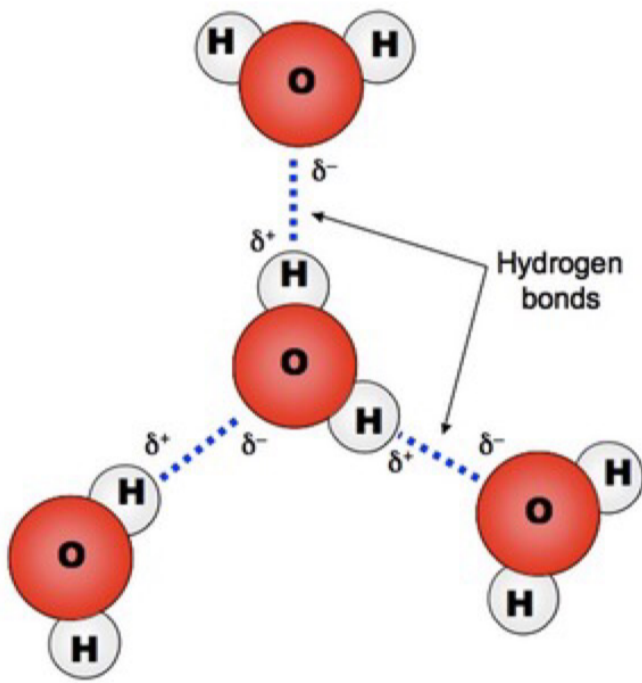
Where R_u is the universal gas constant = 8314 J/Kmol.K

Water is a collection of
water molecules bonded together

It has +ve and -ve charges
allowing the atoms to stick
together forming a molecule



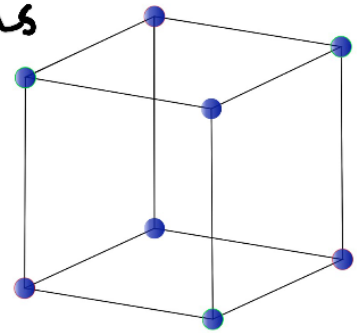
The opposite charges attract each other
and this lets the molecules loosely bond together.



1 Kmol of H_2O molecules
 $= 3 \times 6.022 \times 10^{26}$ Atoms
 (Since 3 atoms per molecule)

Because the atoms are charged,
 they loosely stick together and
 look a bit like a solid.

Each atom has 3 independent directions
 of chemical (Hydrogen) bonds in
 x, y, z directions. The atoms may
 also vibrate in 3 directions.



So each atom has 6 degrees of freedom.

1 Kmol of H_2O has 18 degrees of freedom, since
 each molecule has 3 atoms and each atom has
 6 degrees of freedom.

The internal energy (U) and the Internal energy / Kmol is given by $\bar{U}$.

$$\bar{U} = \text{No of degrees of freedom} \cdot \frac{1}{2} R_u T$$

$\therefore$ The internal energy ($\bar{U}$) of 1Kmol of $H_2O \rightarrow$

$$\bar{U} = 18 \cdot \frac{1}{2} R_u T = 74,826 T \text{ Joules.}$$

Each degree needs an energy of $E = \frac{1}{2} R_u T$ per Kmol

The specific heat @ C_v of H_2O per Kmol $\Rightarrow$

The heat required to raise the internal energy of 1Kmol by 1K.

1Kmol of H_2O has a mass of $[2 \times 1 + 16] = 18 \text{ kg}$

The heat required to make 18kg 1° hotter @ $C_v = 74,826 \text{ J}$

So the heat to make 1kg 1° hotter @ $C_v = 4,157 \text{ J}$

Substance	J/kg°C or J/kg/K	cal/g°C or cal/g/K
Water (0 °C to 100 °C)	4186	1.000
Methyl Alcohol	2549	0.609
Ice (-10 °C to 0 °C)	2093	0.500

Seems about right!



A Dense material has fewer atoms/kg $\therefore$ requires less heat to warm it up. Each atom needs $\frac{1}{2} k_B$ Joules to warm it up 1° /degree of freedom

Bromine gas is a diatomic gas (Br_2) with Molecular weight of $2 \times 79 = 158$.

At room temperature, O_2 has 5 degrees of freedom
3 translational, 2 rotational. $\therefore$

Or $\left\{ \begin{array}{l} \text{O}_2 / \text{Kmol} \Rightarrow \bar{u} = \frac{5}{2} R_u T \\ \text{Specific heat @ } C_v / \text{Kmol} = \frac{5}{2} R_u \end{array} \right.$

So why does Bromine ($\text{Br}-\text{Br}$) have $\bar{u} = \frac{7}{2} R_u T$?



At low temperatures the bromine atoms start to vibrate on the chemical bond, like it is a spring

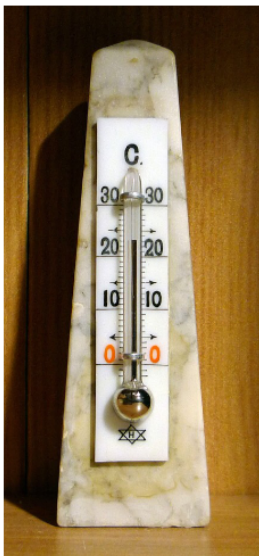
The greater mass of Br means that Br has a lower frequency at which it resonates.

This low frequency can get excited at lower temperatures. There are 2 additional degrees of freedom when a diatomic molecule begins to vibrate.

1. Kinetic energy (2 atoms moving together/apart)
2. Potential energy (Spring Compression/Extension of bond)

Specific heat at C_v of 1 kmol of a gas
= No of degrees $\cdot \frac{1}{2} R_u$

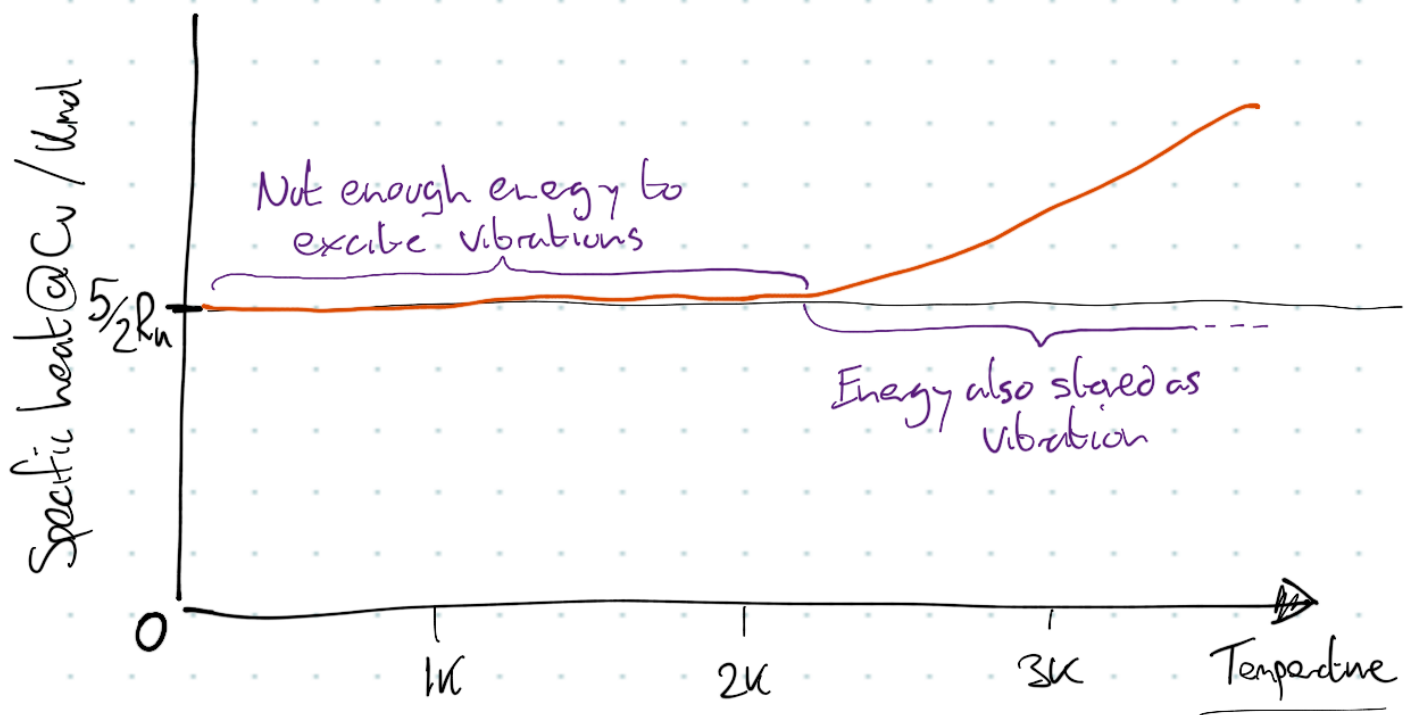
Each degree of freedom must store, on average,
the same Energy.



The thermometer!

This measures the average translational K.E. of the molecules.
(its the molecules hitting the thermometer)

So to put the temperature of the gas up we need to make the molecules move faster. you also put energy into the other degrees of freedom.



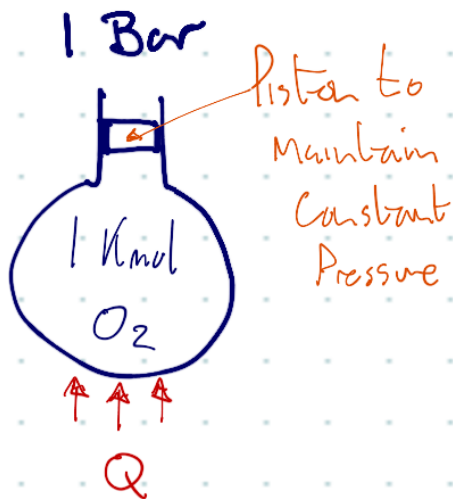
Constant Volume



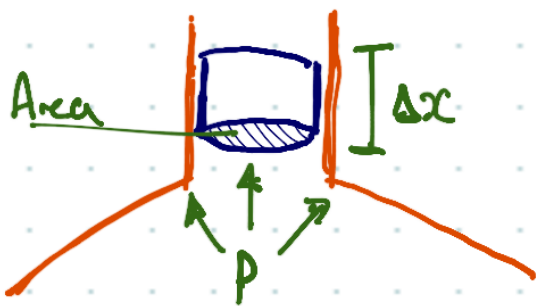
Heat required to raise 1 Kmol / Degree
Hotter @ Constant Volume

$$\bar{C}_v$$

Constant Pressure



To keep the pressure constant
we allow expansion by a
moving piston.



force on the piston from pressure
 $F = P.A.$ (Pressure $\times$ Area)

Work Done moving the piston to
maintain pressure

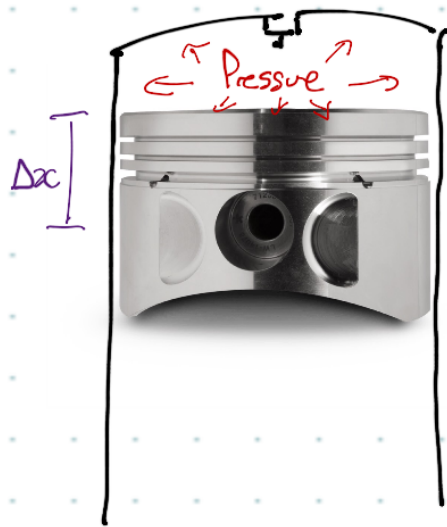
$$WD = F \times \Delta x = P.A.\Delta x = P.\Delta V \quad (P dV)$$

This is the same for a piston
in an engine

$$\text{Force} = \text{Pressure} \times \text{Area}$$

$$\text{WD} = \text{Pressure} \times \Delta V$$

important to
Remember!



Now let's go back to the ideal gas law

$$PV = nR_u T$$

$$\Delta PV = \Delta(nR_u T)$$

At constant pressure

$$P \Delta V = n R_u \Delta T$$

constant

constant

To warm 1 kmol by 1° at constant pressure
($n=1$, $\Delta T=1$)

$$\text{WD} = P \Delta V = 1 \cdot R_u \cdot 1 = R_u$$

$$P \Delta V = R_u = \text{WD}$$

The heat required to: $(\bar{C} : \text{molar specific heat})$

Heat 1 kmol by 1° at constant Volume $= \bar{C}_v$

Heat 1 kmol by 1° at constant pressure $= \bar{C}_v + R_u$

$$\therefore \bar{C}_p = \bar{C}_v + R_u \quad \text{This is important!}$$

You have to make both equally hot, but at constant pressure you also have to do work on the boundaries.

Number of kg in a kmol = Molecular weight

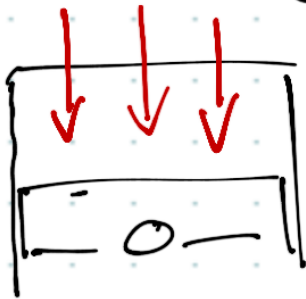
$$\frac{\bar{C}_p}{\text{Mol wt}} = \frac{\bar{C}_v}{\text{Mol wt}} + \frac{R_u}{\text{Mol wt}}$$

These become the Specific heats / kg

$$C_p = C_v + R$$

$$\text{and } R = \frac{R_u}{\text{mol wt}} = \text{Gas constant / kg}$$

First law of thermodynamics says 'if you put heat into a gas'...



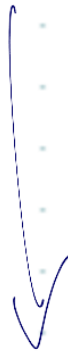
$$\Delta u = M C_v \Delta T$$

or $\Delta u = n \bar{C}_v \Delta T$

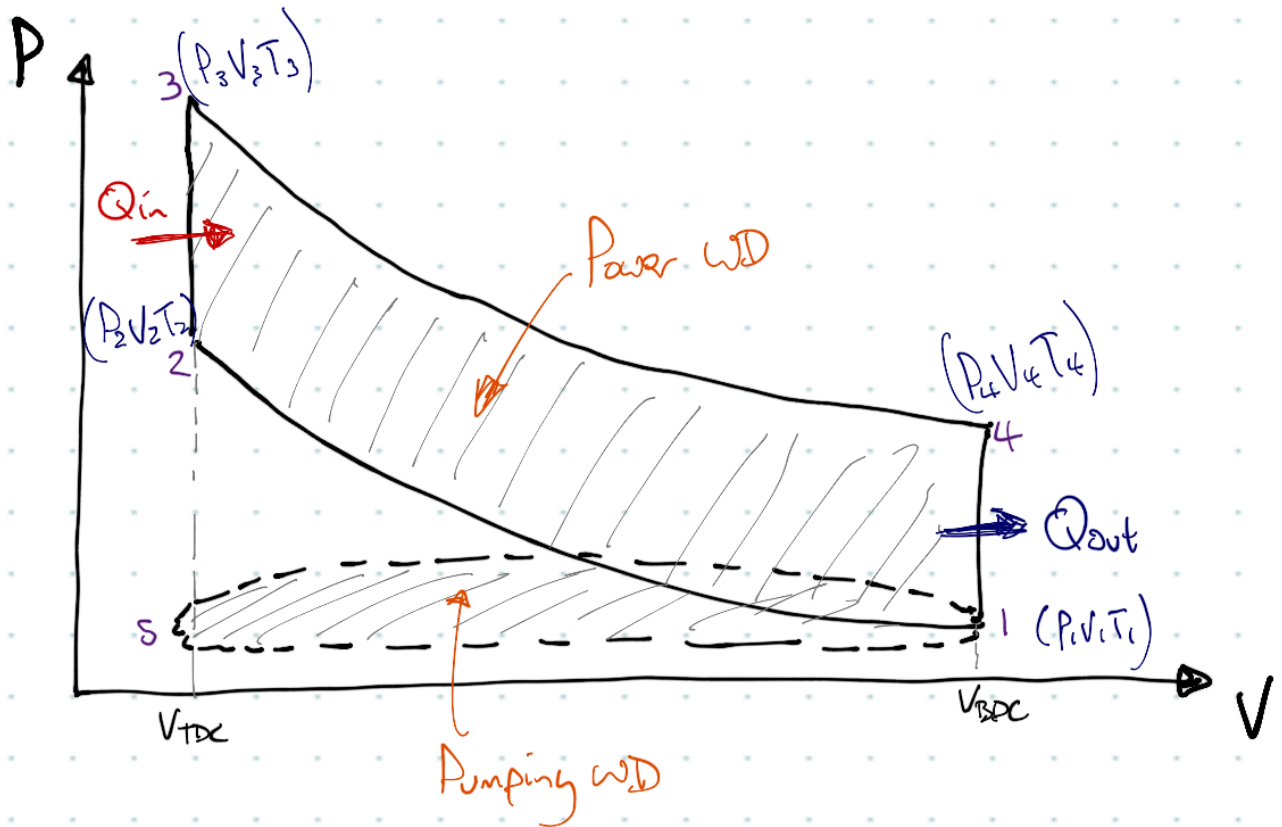
$$\Delta Q = \Delta u + P \Delta V$$

Related to temp
increase

Related to
boundary work



Lets look at the ideal 'Otto cycle'



Power loop

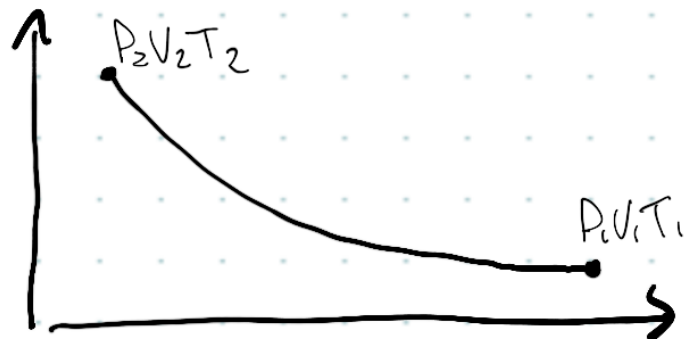
- 1-2 Adiabatic Compression [no heat loss]
- 2-3 Constant Volume, Heat in
- 3-4 Adiabatic Expansion
- 4-1 Constant Volume, Heat out

Pumping loop

- 1-5 Pushing exhaust out
- 5-1 Suckling air in

Net WD = Area of Power loop - Area of pumping loop

Equation for Adiabatic Compression?



$$\Delta Q = \Delta u + P \Delta V$$

$$\Delta Q = M C_v \Delta T + P \Delta V$$

for adiabatic $\rightarrow \Delta Q = 0$

So Adiabatic First law

$$0 = M C_v \Delta T + P \Delta V$$

Now look at $P \cdot V = n R T$

$$\therefore \Delta P V = \Delta n R T = n R \Delta T - \textcircled{1}$$

$$\Delta P \cdot V = (P + \Delta P)(V + \Delta V) - P \cdot V$$

$$\Delta P \cdot V = \cancel{P \cdot V} + P \Delta V + V \Delta P + \Delta P \Delta V - \cancel{P \cdot V}$$

$$\Delta P V = P \Delta V + V \Delta P + \underbrace{\Delta P \Delta V}$$

In Calculus, we assume $\text{small} \times \text{small} = \text{negligibly small!}$

$$\therefore \Delta P V = P \Delta V + V \Delta P = n R \Delta T$$

From above $\Delta T = \frac{\Delta P V}{n R}$ From $\textcircled{1}$

$$0 = n C_v \Delta T + P \Delta V$$

So

$$0 = \frac{\cancel{n C_v} (P \Delta V + V \Delta P)}{\cancel{n R}} + P \Delta V$$

$$0 = \frac{C_v}{R} \cdot (P \Delta V + V \Delta P) + P \Delta V$$

Now from $C_p = C_v + R$... divide by C_v

$$\frac{C_p}{C_v} = \frac{C_v}{C_v} + \frac{R}{C_v}$$

Ratio of
Specific heats
↓
↓

$$\gamma = 1 + \frac{R}{C_v}$$

$$(\gamma - 1) = \frac{R}{C_v}$$

So

$$0 = \frac{P \Delta V + V \Delta P}{(\gamma - 1)} + P \Delta V$$

multiply both sides by $(\gamma - 1)$

$$0(\gamma-1) = P\Delta V + V\Delta P + (\gamma-1)P\Delta V$$

$$0 = \cancel{P\Delta V} + V\Delta P + \gamma P\Delta V - \cancel{P\Delta V}$$

$$0 = V\Delta P + \gamma P\Delta V \quad \text{Divide by } PV$$

$$\frac{0}{PV} = \frac{\cancel{V}\Delta P}{\cancel{P}V} + \gamma \frac{\cancel{P}\Delta V}{\cancel{P}V}$$

$$0 = \frac{\Delta P}{P} + \gamma \frac{\Delta V}{V}$$

Now we need to
integrate this!

$$\int 0 = \int \frac{\Delta P}{P} + \gamma \int \frac{\Delta V}{V}$$

$$C = \ln P + \gamma \ln V$$

$$C = \ln P + \ln V^\gamma$$

$$C = \ln PV^\gamma$$

So ... $PV^\gamma = \text{Constant!}$