

More Fundamental Thermodynamics

Molecules move when above absolute zero (-273°C)
In a solid, they vibrate. In a gas, they move around.
The KE_{Av} of a molecule in the x direction is:

$$\frac{1}{2} M V_x^2 = \frac{1}{2} K_B T$$

M = mass of molecule

V_x = Average velocity of molecule in the x direction

$K_B = 1.38 \times 10^{-23} \text{ J/Kg} \cdot \text{K}$ (Boltzmann's constant)

If we multiply both sides by 6.022×10^{23} [Avogadro's No.]

$6.022 \times 10^{23} \times M = \text{Molecular weight in Kg.}$

(Discuss atomic structure) ...

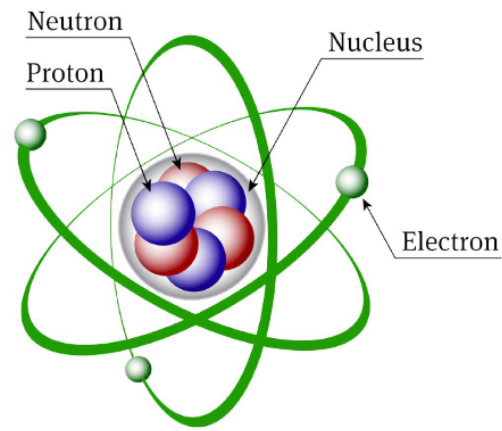
See periodic table

Lead (Pb) Atomic number = 82

Mass number = 207

Gold (Au) Atomic number = 79

Mass number = 197



Gold has a nucleus of 79 protons and $(197 - 79)$ 118 neutrons.

Lead has a nucleus of 82 protons and 125 neutrons

$\therefore$ 'Alchemy' is not possible without Nuclear Physics!

For lead - 6.022×10^{26} atoms weighs 207 kg

For gold - 6.022×10^{26} atoms weighs 197 kg

For Hydrogen - 6.022×10^{26} atoms weigh 2 kg

$$6.022 \times 10^{26} \times \frac{1}{2} m v_{rc}^2 = 6.022 \times 10^{26} \times \frac{1}{2} k_B T$$

$$\frac{1}{2} \cdot \text{molecular weight (kg)} \times v_x^2 = \frac{1}{2} \times 6.022 \times 10^{26} \times (1.38 \times 10^{-23}) T$$

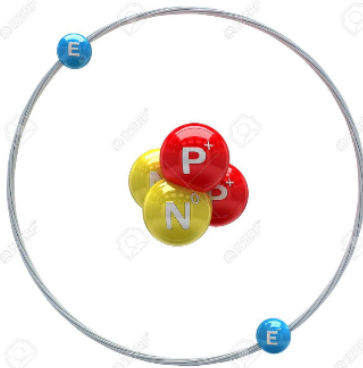
$$\Rightarrow 6.022 \times 10^{26} \times 1.38 \times 10^{-23} = 8310.36$$

Some rounding errors $\dots \Rightarrow 8314 \text{ J/mol.K}$

We call this $R_u \rightarrow$ universal gas constant

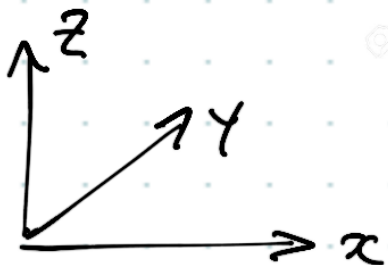
The average KE of a K.mol of stuff in the x direction
 $= \frac{1}{2} R_u T$

For Helium:



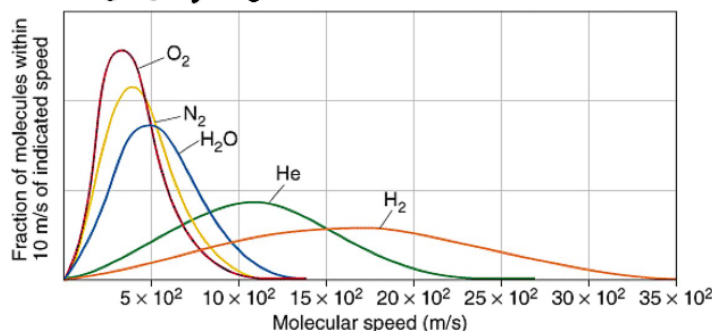
Helium is a gas of 'atoms'
 (Inert gas)

He } Monatomic gases
 Ne } (exist as atoms)
 Ar }



$$KE_{Av x} = KE_{Av y} = KE_{Av z}$$

Total KE for 1 K.mol of Helium $= 3 \times \frac{1}{2} R_u T$
 What can we use this for?



$$\frac{1}{2} m v^2 = \frac{3}{2} R_u T \quad \text{so}$$

$$v^2 = \frac{3 R_u T}{M}$$

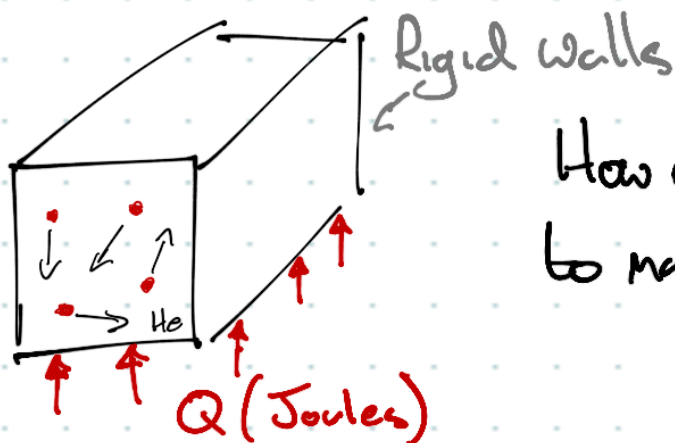
$$v^2 = \frac{3 \times 8314 \times 298}{14}$$

(Nitrogen gas)

$$v = 728 \text{ ms}^{-1} \sim 1626 \text{ mph}$$

Nice!

What else?



How much energy do you need to make 1 k.mol 1 K hotter?

$$\text{Total KE of 1 k.mol After} = \left[\frac{3}{2} R_u (T+1) \right]$$

$$\text{Total KE of 1 k.mol Before} = \left[\frac{3}{2} R_u T \right]$$

$$\Delta \text{KE} \equiv \text{Heat required.} \quad (\text{After} - \text{Before})$$

$$\frac{3}{2} R_u T + \frac{3}{2} R_u (1) - \frac{3}{2} R_u T$$

$$\text{Therefore, Heat required} = \frac{3}{2} R_u$$

$$= 12,471 \text{ J}$$

$$\therefore \text{Specific heat of Helium / K.mol @ Constant Volume}$$

$$= \bar{C}_v (C_v \text{ molar}) = \underline{12,471 \text{ J/K.mol.K}}$$

$$1 \text{ Kmol of Helium} = 4 \text{ Kg}$$

$$\therefore \text{Specific heat in J/Kg.K} = 12,471 / 4$$

$$= \underline{3117 \text{ J/Kg.K}}$$

$$\text{Average KE of one K.mol of Helium (or Neon or Argon)}$$

$$= \frac{3}{2} R_u$$

$$\text{Heat required to raise 1 K.mol of the above gases}$$

$$\text{by 1K @ } C_v = \frac{3}{2} R_u \text{ [monatomic gases]}$$

$$\text{Argon Atomic weight} = 40$$

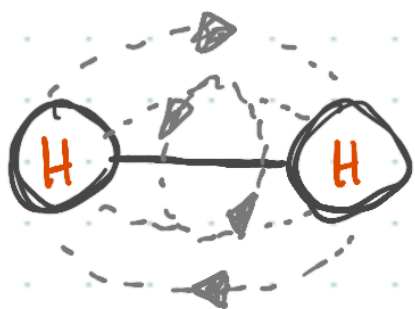
$$\text{Heat required to raise 1Kg by 1K} = \frac{\frac{3}{2} R_u}{40}$$

$$= 312 \text{ J/Kg.K.}$$

Hydrogen is Diatomic (H_2) - Molecule of 2 atoms
(Also true for O_2 and N_2)

For Hydrogen Av KE / K.mol in all directions = $\frac{3}{2} R_u T$

Consider H_2 as 'moving lumps'. The moving lumps have the same average KE regardless of molecule size



H_2 has 3 rotational axes
 H_2 only has 2 Significant MOI's that can store energy.

Rotations around the bond axis lacks MOI $\therefore$ it does not effectively store energy.

Quantum Mechanics - Equipartition of energy

Each degree of Freedom has the same Av. KE.

Call KE in x direction $\rightarrow$ 1 degree of freedom
" y " $\rightarrow$ "
" z " $\rightarrow$ "

Rotational about z - 1 degree of freedom
 " y - "
 " z - "

So Hydrogen (H_2) has a total of 5 degrees of freedom

3 x Translational 2 x rotational

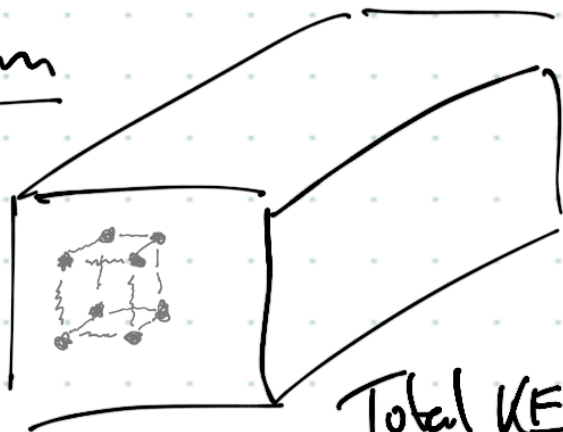
Each degree of freedom has $KE = \frac{1}{2} R_u T / \text{Kmol}$

Total stored energy in 1 K.mol $H_2 = \frac{5}{2} R_u T$

$\frac{5}{2} R_u$ to make 1 K.mol of H_2 1 K hotter

$$= 20,785 \text{ J/Kmol.K}$$

Aluminium



Each atom in a solid will vibrate in x, y, z directions.

3 degrees of freedom in vibration

$$\text{Total } KE_{av} = \frac{3}{2} R_u T$$

But each atom also has 3 degrees of 'Potential energy' Freedom i.e. you can compress 3 different springs!

$$\text{Total PE/Kmol} = \frac{3}{2} R_u T$$

So all solids have 6 degrees of freedom ~

$$\therefore \text{Stored energy / K.mol} = \frac{6}{2} R_u T$$

Energy required to raise 1 K.mol of Solid 1K hotter

$$3 R_u (T+1) - 3 R_u T = 3 R_u = 25,000 \text{ J/K.mol}$$

This is the specific heat for 1 K.mol of a solid,
Since it has 6 degrees of freedom.

Atomic wt of AL = 27

$$\text{Specific heat / Kg} = \frac{25,000}{27} = 923 \text{ J/Kg.K}$$

Steel (Fe) atomic weight = 56

$$\text{Specific heat / Kg} = \frac{25,000}{56} = 446 \text{ J/Kg.K}$$

Important!

Because Aluminium is less dense, it has MORE atoms / Kg to heat up!

Remember:

for Anything ~

The average KE / degree of freedom / Atom = $\frac{1}{2} k_B T$

The same for ALL atoms

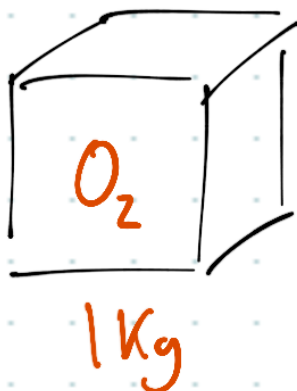
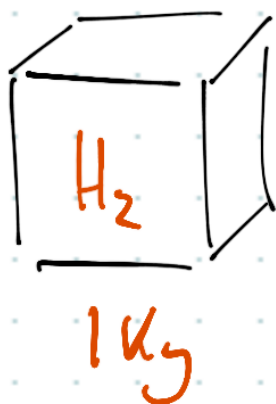
To warm something up, you have to increase the KE of every atom by the same amount. The more atoms/kg, the more heat you need to warm it up



The number of atoms/cc
in most solids is the same!

i.e. The distance between most atoms
in a solid is roughly constant ---

$\therefore$ Heavier nucleus $\Rightarrow$ Density



How much more heat
is needed to raise
 H_2 by 1K than O_2
?

Things to remember:

$$1 \text{ mole} = 6.022 \times 10^{23} \text{ things}$$

For Nitrogen (Atomic mass 14) 6.022×10^{23} atoms $\rightarrow 14\text{g}$

$$6.022 \times 10^{26} \text{ atoms} = 14 \text{ kg}$$

Universal gas constant $R_u = 6.022 \times 10^{26} \times 1.38 \times 10^{-23}$

$$R_u = 8314 \text{ J/K.mol.K}$$

Note the difference from the 'Specific gas constant'
for the assignment you would have used

$$\underline{R_{air} = 287.05 \text{ J/kg.K.}}$$

How are these related?

Where does specific heat capacity fit in?

Find out Next week!

Homework Solutions

$$\begin{aligned}\text{Energy to heat } H_2 \text{ by } 1K &= \frac{5}{2} R_u \\ &= 20,785 \text{ J/K.mol.K}\end{aligned}$$

$$\begin{aligned}\text{Specific heat /kg } (H_2) &= \frac{20,785}{2} \\ &= 10,392.5 \text{ J/kg.K}\end{aligned}$$

$$\begin{aligned}\text{Specific heat /kg } (O_2) &= \frac{20,785}{16} \\ &= 1299 \text{ J/kg.K}\end{aligned}$$

So $10392 - 1299 = 9093 \text{ J/kg.K}$ More
needed to heat 1Kg of H_2 than O_2
