Lecture 5

19-7 Molar specific heats of an ideal gas

- Goal is to derive an expression for internal energy of an ideal gas, from molecular considerations
- 1st assume that ideal gas is monatomic (consists of single kind of atom)
  helium, neon, etc.

- internal energy E_{int} is sum of translational kinetic energies of atoms
- For a single atom, the average is $K_{avg} = 3/2\, kT$
- A sample of n moles contains nN_A atoms $\Rightarrow E_{int} = (nN_A) K_{avg} = nN_A \cdot \frac{3}{2} kT$

Using $k = \frac{R}{N_A}$

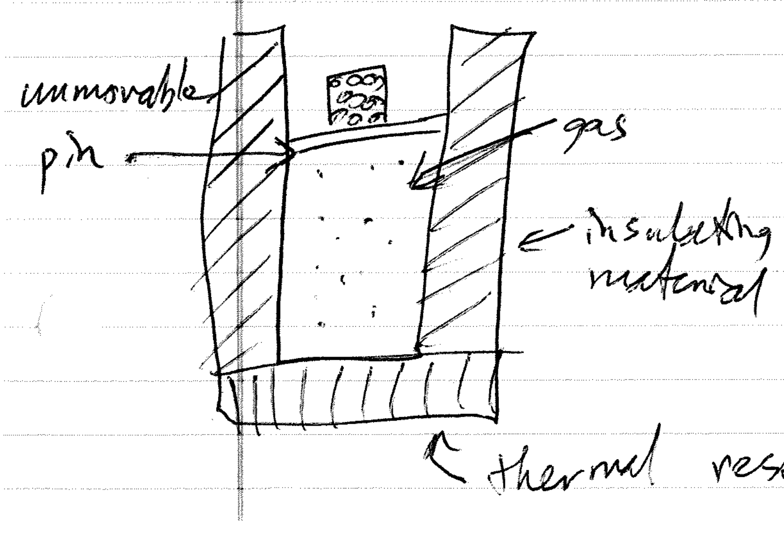
$$\Rightarrow \boxed{E_{int} = \frac{3}{2} nRT}$$

for monatomic ideal gas

function of temperature only

- We can now derive an expression for molar specific heat
  1) when volume is constant - C_V
  2) when pressure is constant - C_p

Consider 1) first



n moles of ideal gas @ pressure p + temp. T @ fixed volume V.

Turn up temperature & transfer heat, then found experimentally that

$$Q = n\, C_V\, \Delta T$$

heat — # of moles — molar specific heat @ constant volume — change in temp.

Substitute into 1st law of thermo, to get

$$\Delta E_{int} = Q - W$$
$$= n\, C_V\, \Delta T$$

(W = 0 for constant volume)

$$\Rightarrow \quad C_V = \frac{\Delta E_{int}}{n\, \Delta T}$$

From our expression for internal energy, we find that

$$\Delta E_{int} = \frac{3}{2} n R \Delta T$$

(monatomic gas)

$$\Rightarrow \quad C_V = \frac{\frac{3}{2} n R \Delta T}{n \Delta T}$$

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

$$\Rightarrow \quad \boxed{C_V = \frac{3}{2} R} = 12.5 \frac{J}{mol \cdot K}$$

It is different for diatomic & polyatomic gases (involving molecules w/ more than one atom)

- these have rotational kinetic energy

we can then back substitute & ~~find~~ that

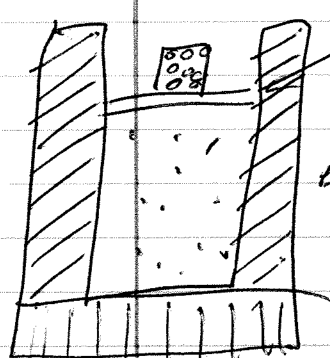
$$E_{int} = \frac{3}{2} n R T = n C_V T$$

then change in internal energy for confined (constant volume) ideal gas is

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

Molar specific heat @ constant pressure

- Suppose temp. increased by small amount but now heat is added under constant pressure



heat Q related to temp. change by

$$Q = n\, C_p\, \Delta T$$

heat — Q; # of moles — n; molar specific heat @ constant pressure — C_p; change in temp. — ΔT

Goal now is to relate C_p + C_V:

Start w/ 1st law of thermo:

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

For ΔE_{int}, we can substitute

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

For Q, substitute $Q = n C_p \Delta T$

For W, set $W = p \Delta V$

$$= \underbrace{n R \Delta T}_{\text{from ideal gas equation}}$$

$$\Rightarrow \quad n C_V \Delta T = n C_p \Delta T - n R \Delta T$$

$$\Rightarrow \quad C_V = C_p - R$$

$$\Rightarrow \quad \boxed{C_p = C_V + R}$$

how molar specific heat @ constant pressure is related to molar specific heat @ constant volume.

$\Rightarrow$ relative value of Q for a monatomic gas undergoing constant-volume process: $Q = \frac{3}{2} nR\Delta T$

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

or constant-pressure process: $Q = \frac{5}{2} nR\Delta T$

$(C_p = \frac{5}{2}R)$

Degrees of freedom & molar specific heats

$C_V = \frac{3}{2}R$ agrees w/ experiment for monatomic gases, but does not work for diatomic & polyatomic gases.

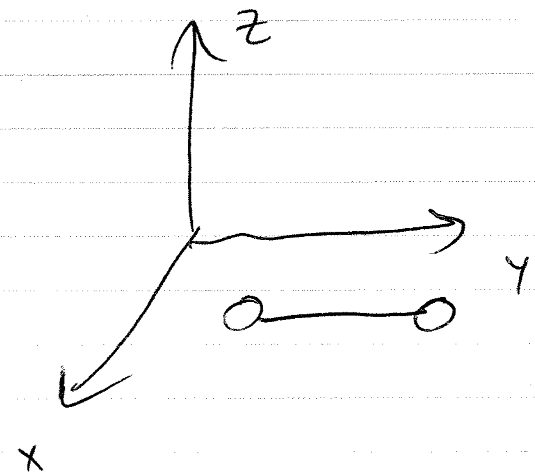
- The reason is that diatomic & polyatomic gases have other forms of kinetic energy besides translational.
- They can also have rotational energy, due to rotational motion

- consider monatomic gas helium; it can move in x, y, z directions, but does not have rotational energy

 ← He

- oxygen O_2, a diatomic molecule containing two atoms of oxygen looks like 

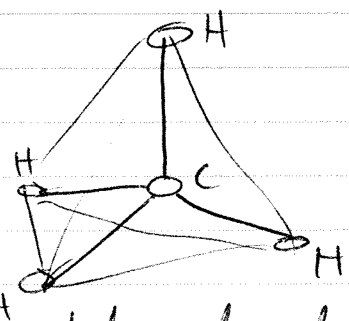
- it can move in x, y, z directions
  & has 3 degrees of freedom
- it can also rotate about
  x & z axis,
  but not y
  axis.



So it has 2 rotational degrees of freedom

then 5 in total

- methane (CH_4) is a polyatomic molecule



has 3 translational degrees of freedom & 3 rotational degrees of freedom then 6 DoF in total.

<u>Important observation of Maxwell called "Equipartition of energy"</u>:

- Every molecule has a certain number f of degrees of freedom (DoF), which are independent ways in which the molecule can store energy.
- Each DoF contributes an average energy of $\frac{1}{2}kT$ per molecule

$\Rightarrow$ extension of molar specific heats to ideal diatomic & polyatomic gases

$\Rightarrow E_{int} = \frac{f}{2} nRT \Rightarrow C_V = \frac{f}{2} R$