Predicting on basis of Theoretical model

2 out comes

① Experiment is as expected

② Experiment UNEXPECTED

② → may be more interesting

TEXTBOOK → DEGREES OF FReedom FREEZE OUT

MAJOR PUZZLE OF 19TH Century Science

⇒ Why did Einstein work on Specific Heats? → BORING

→ Quantum Mechanics.

Here is Puzzle

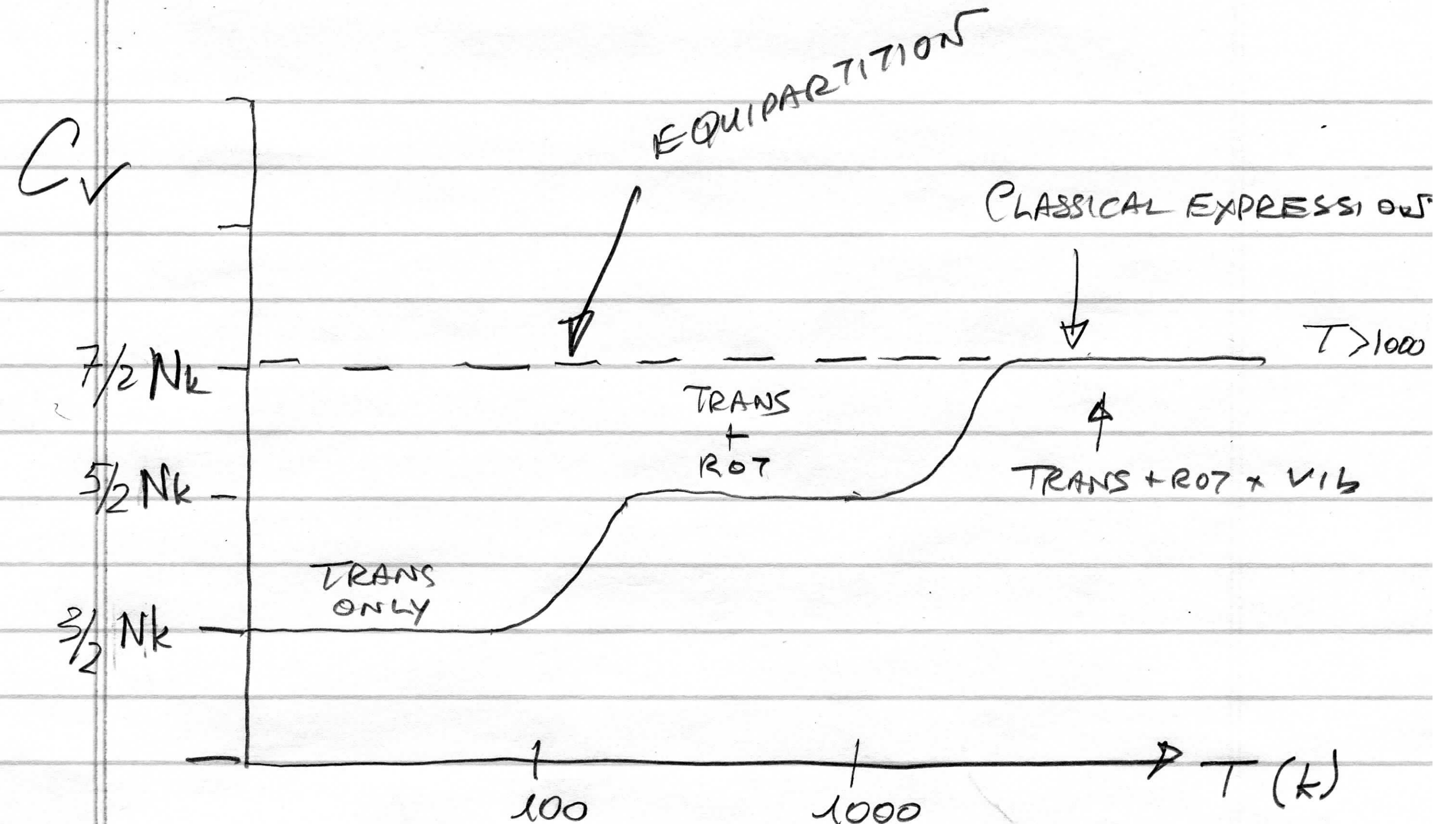
Heat Capacity C_V of diatomic molecule (eg H_2) comes from equipartition of total energy of the gas

$$U = \frac{NkT}{2}\left(\underbrace{3}_{\text{TRANS}} + \underbrace{2}_{\text{ROT}} + \underbrace{2}_{\text{vib}}\right)$$

vib: $1 \times kT$ or $2 \times \frac{kT}{2}$

So $C_V = Nk\left(\frac{3}{2} + \frac{3}{2} + \frac{2}{2}\right) = 7Nk$

$\left(\frac{\partial u}{\partial T}\right)_P$



Cannot be understood classically

CLASSICALLY ROT + VIB degrees of freedom can carry arbitrarily small amounts of energy

2 molecules colliding — no matter how small kT

↓

some energy into ROT + VIB

All dof carry same ENERGY ~ kT on AVERAGE ←

↳ they do <u>NOT</u>

Maxwell noted this problem in his first paper on KINETIC GAS THEORY 1859

"NOT possible to satisfy known specific Heats"

1869 "---- greatest difficulty of the molecular theory ----"

Quantum mechanics is the answer.

ROTATION — ANGULAR MOMENTUM QUANTIZED

— comes in packets of

$0, \hbar, 2\hbar, 3\hbar \ldots$

(funnily electron is $\frac{\hbar}{2}$!)

Ang MOM $= L = I \dot{\phi}$

moment of INERTIA

ANGULAR VELOCITY

$$L = I\dot{\phi}$$

$$\text{ENERGY} = \frac{I\dot{\phi}^2}{2} = \frac{1}{2I}\cdot\left(I\dot{\phi}\right)^2 = \frac{L^2}{2I}$$

in QM MINIMAL ROTATIONAL ENERGY CHANGE

$$0 \longrightarrow \frac{1\hbar^2}{2I}$$

FOR H_2 MOLECULE

2 BOHR RADII

0.7×10^{-10} m

MASS 10^{-27} kg

SO $I = 10^{-27}\left(0.7\times10^{-10}\right)^2$

2 MASSES

$kg \cdot m^2$

$$I = 5\times10^{-47}\ kg\cdot m^2$$

MINIMUM ROT ENERGY $\sim \frac{\hbar^2}{I}$

$$\sim \frac{\left(10^{-34} \frac{m^2 kg}{s}\right)^2}{10^{-48} kg\, m^2}$$

$$E_{ROT} = \frac{10^{-68}}{10^{-48}} \frac{m^4 kg^2}{s^2 kg\, m^2} \sim 10^{-20} \frac{m^2 kg}{s}$$

this is an energy so in Joules.

$$E^{ROT}_{MIN} = 10^{-20} J$$

Translational energy

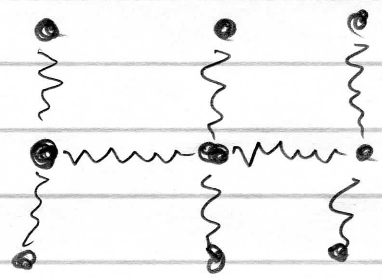
$$kT \sim 10^{-23} J \times T \left(m^2 kg\, s^{-1} K^{-1}\right)$$

k

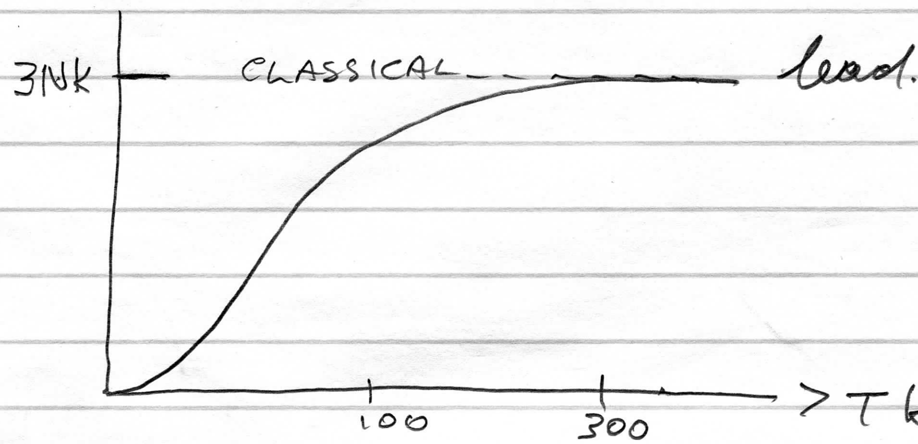
For $T > 1000k$ reach min rot energy.

$kT \ll E^{ROT}_{MIN} \longrightarrow$ COLLISIONS DO NOT EXCITE ROTATIONA ENERGY

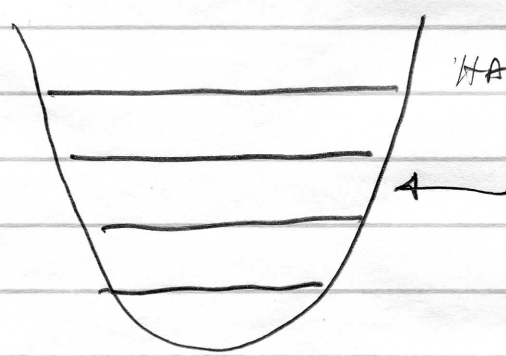
SPECIFIC HEAT OF SOLIDS



HARMONIC OSCILLATORS



QUANTUM HARMONIC OSCILLATOR



energy levels spaced by $\sim \hbar\omega$

$\hbar\omega \gg kT$

for $T \sim 100K$

at low temp

VERY UNLIKELY TO GO FROM GROUND STATE