23/10/09

Lecture 24

Odds & Ends

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Things I wanted to do but ran out of time

Tds Equations

Derived from:

$$T\,ds = du + P\,dv$$

→ 3 "Tds eqns"

for $s = s(T, v)$

$$\rightarrow \quad T\,ds = c_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$$

$$= c_v\,dT + \frac{T\beta}{\kappa}\,dv$$

for $s = s(T, P)$

$$T\,ds = c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$$

$$= c_p\,dT - Tv\beta\,dP$$

for $s = s(v, P)$

$$T\,ds = c_p \left(\frac{\partial T}{\partial v}\right)_P dv + c_v \left(\frac{\partial T}{\partial P}\right)_v dP$$

$$= \frac{c_p}{\beta v}\, dv + \frac{c_v K}{\beta}\, dP$$

where $\beta \equiv$ Expansivity $\equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$

$K \equiv$ Isothermal compressibility $\equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$

EQUIPARTITION of ENERGY,
Degrees of freedom & γ

At eqm, energy is distributed equally between all degrees of freedom with

$$\langle \text{Energy of mode} \rangle = \frac{1}{2} kT$$

For monatomic gas, three degrees of freedom: v_x, v_y & v_z

$$\Rightarrow \langle \tfrac{1}{2} m v_x^2 \rangle = \tfrac{1}{2} kT$$

$$\Rightarrow \langle \tfrac{1}{2} m v^2 \rangle = \tfrac{3}{2} kT$$

Diatomic molecule:

Classically: 7 degrees of freedom : 3 transl. KE
+ 2 rot^n KE
+ 2 vibrat^n [KE + PE]

1 vib = 2 since PE + KE

QM : 7 degrees of freedom : 3 trans
2 rot^n
2 vib

~~(can think of these 1 f but steps are kT not ½ kT)~~

$\therefore$

$$U = N \cdot (\text{Average energy/particle})$$

$$= f \cdot N \cdot \tfrac{1}{2} kT$$

↑ # degrees of freedom

$$\Rightarrow \boxed{U = \frac{f}{2} nRT}$$

But recall, for ideal gas:

$$U = \frac{1}{\gamma - 1} \cdot nRT \quad !$$

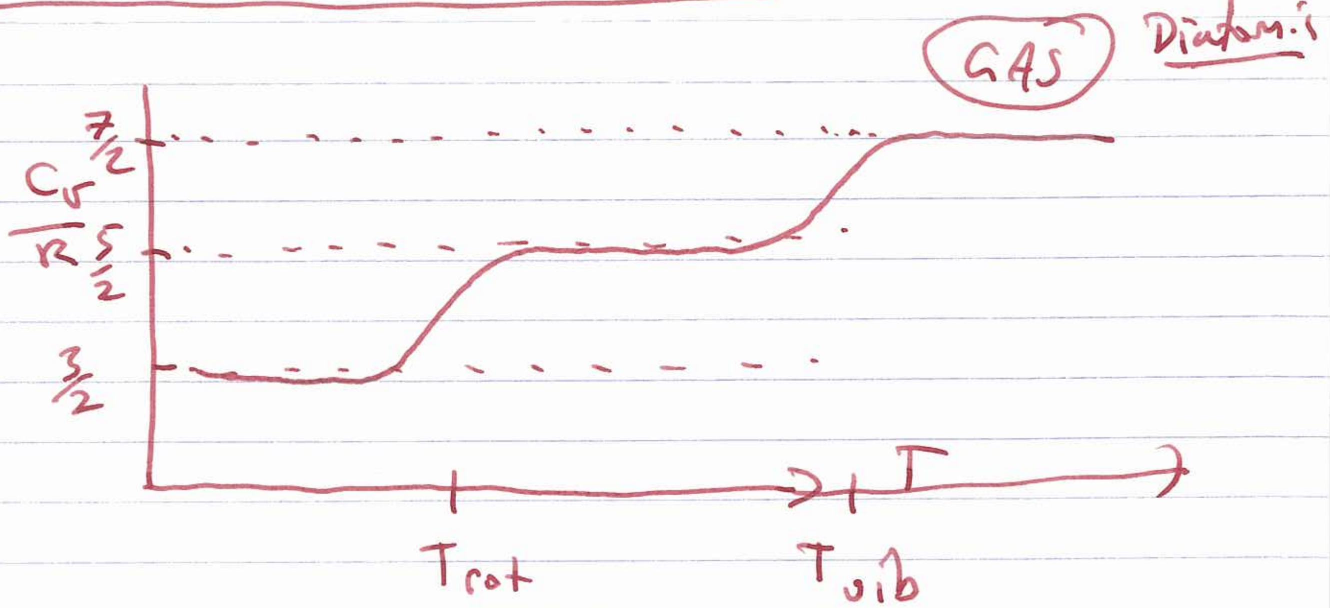
$$\Rightarrow \boxed{\gamma = \frac{c_p}{c_v} = \frac{f+2}{f}}$$

& for ideal gas:

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

$$c_p = \left(\frac{f+2}{2}\right) R$$

More QM weirdness



⇒ Below T_{rot}, only translation motion

Below T_{vib}, only trans & rotn

CO $T_{rot} \simeq 2.8K$

$T_{vib} \simeq 3103K$ (!)

DEMONSTRATION

Belousov-Zhabotinsky Reaction

Discovered by Belousov in early 50's & no one believed it possible

Zhabotinsky developed theory in 60's

Both USSR

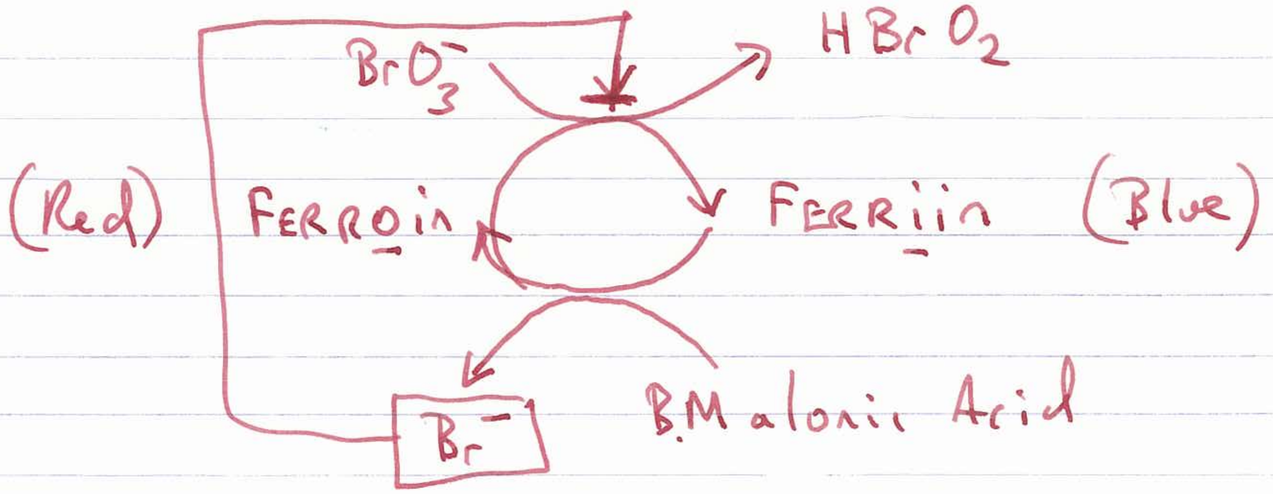
BZ reaction: Non-linear Chemical oscillator

Conditions for form EqM

MECHANISM COMPLEX (!)

~ 40 elementary reactions

Simplified scheme



NEGATIVE Feed back: Br^- inhibits

$BrO_3^- \rightarrow HBrO_2$

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