

Modern Applications of Spectroscopy

ESR, NMR we cancel (no time!)

also elsewhere (e.g. org. chem.)

Laser

first came 1953 the Maser:

microwave amplification by stimulated emission of radiation

later also with other frequencies
including IR, vis., UV

→ Laser

Light ampl. ...

Laser beam:

when excitation energy is pumped
into a system such that a population
inversion appears

normally: much more molecules
populate the ground state than any
excited state

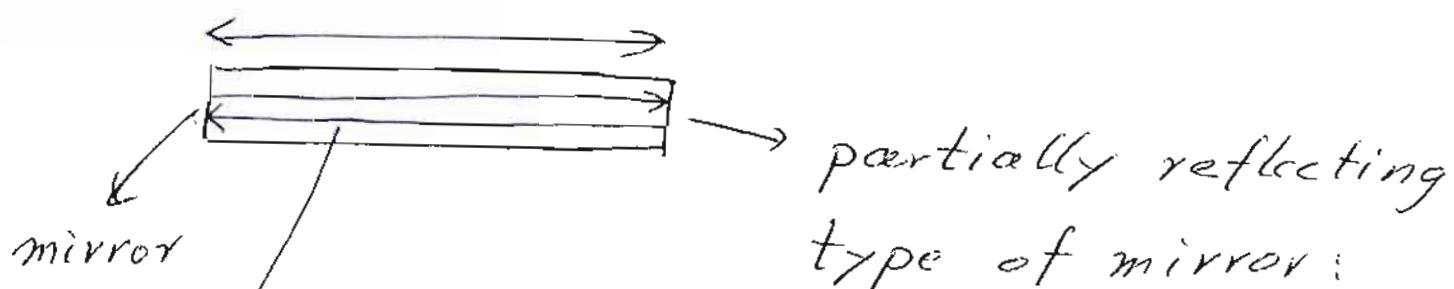
excited molecules can emit light spontaneously (from alone), but also when stimulated by light of the same frequency

light sent into a ^{system} ~~sample~~ with population inversion,

then more stimulated emission than absorption ~~occurs~~ happens.

→ ~~amplification~~ or gain of intensity of the radiation passing through

sample chamber's cavity



light passes several times and become amplified

large enough, light

can pass

$$l = \frac{nd}{2} \text{ for standing wave}$$

→ part of the beam escapes (35)-3
when intensity is large enough

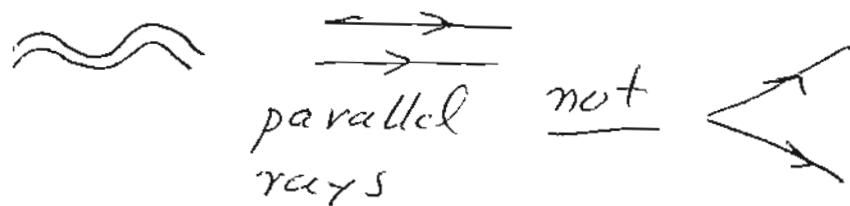
→ laser action

optic are such, that only 1 λ -value
is amplified

if $\frac{n\lambda}{2} \neq l$: destructive interference of
the reflected wave with
itself

→ coherent light:

spatial coherence: all wave trains in
phase across the beam



temporal coherence: the light stays
in phase

e.g. He-Ne lasers: coherent to 10cm
away from lasers

coherence length: for other lasers
much longer than 10cm

coherence length of a normal light bulb: $\approx 100\text{ nm}$

effective Laser action

1. Population inversion created by effective pumping

\rightarrow stimulated emission \gg absorption
 \uparrow
 rates

2. Emitted photons must stimulate enough further emission

\rightarrow use of mirror to keep the light long time inside the cavity

3. Excited state must have a long lifetime (for population inversion)

\rightarrow metastable excited state

usually: excitation \rightarrow excited state

\downarrow
 goes into a metastable excited state with long lifetime
 \rightarrow pop. inversion

some types of Lasers

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Solid state Lasers

e.g. ruby = Al_2O_3 with a few Cr^{3+} ions
(≈ 1 out of 100 - 1000)
instead of Al^{3+}

Xe flash lamps around a ruby rod
 \rightarrow inversion

Xe photons ~~are from~~ lead to
an $^4A_2 \rightarrow ^4F_1, ^4F_2$ excitation in ruby
with fast, non-radiative decay
to a 2E state

2E is long living
 \rightarrow many atoms remain for long
in $^2E \rightarrow$ inversion

3 state Laser

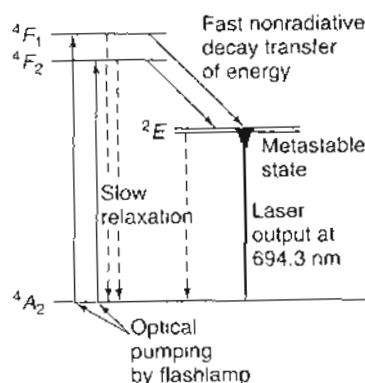


FIGURE 14.3
Energy levels in a ruby laser showing transitions resulting in occupancy of the metastable state 2E with subsequent laser output in a typical three-level laser

it covers a very narrow range of wavelengths). Also, if the laser medium (ruby) has a suitable geometry, the beam divergence can be extremely small of the order of a milliradian, and is coherent.

Another solid-state laser is the **neodymium laser**. It normally is formed Nd^{3+} ions in low concentration in a yttrium aluminum garnet and is then known as a *YAG laser*. This laser operates in the infrared most efficiently at 1060 nm. The energy scheme for this *four-level laser* is shown in Figure 14.4. In this more efficient transfer of energy exists in which the higher excited metastable state emits to a lower excited metastable state which is initially empty or only populated. Often *frequency doubling* is used (see page 657), the beam being converted into radiation with double its initial frequency. The wavelength is then 532 nm in the green region of the visible spectrum.

Several **gas lasers** are commonly used and can generate high power, since the generated heat produced in the excitation process is easily dissipated by the rapid passage of gas through the cavity. In the **helium-neon laser**, helium atoms are excited by an electric discharge to the metastable $1s^12s^1$ configuration, as shown in Figure 14.5. Transitions by such discharges are not restricted by selection rules. Energy is transferred through collisions to neon which has excited states of appropriate energy. In effect, upper levels are heavily populated by the transfer, whereas the lower levels have the lower normal number of electrons as determined by the Boltzmann distribution. There is thus a population inversion, and lasing action occurs at 632.8 nm and at several other wavelengths.

The **carbon dioxide laser** also uses an energy exchange. In this device carbon dioxide is vibrationally excited by an electric discharge and again there are no symmetry restrictions. This energy is transferred through electronic exchanges and ionic collisions to the v_3 antisymmetric stretching vibrational levels of CO_2 , as shown in Figure 14.6. The laser action takes place between the lowest excited level of the v_3 vibration and the lowest excited level of the symmetric stretch v_1 . The strongest emission occurs at 10.59 μm , with a second emission possible at 9.6 μm .

Both **argon-ion** and **krypton-ion** lasers operate on the same principle. An electric discharge is passed through the working gas held at a pressure of

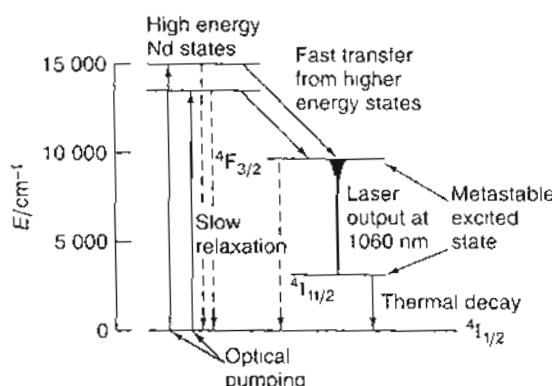


FIGURE 14.4
Energy levels in a neodymium laser showing transitions resulting in occupancy of the metastable state $^4F_{3/2}$. This state has a lifetime of 5×10^{-4} s before dropping to the $^4I_{11/2}$ state which is populated only slightly by thermal electrons. This is an example of a four-level laser.

some lasers are continuous
wave (cw) ones

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others emit short (ns) pulses of laser
light

~~very~~ power in pulsed lasers up
to $1 \text{ GW} = 10^9 \text{ W}$

(short time, not too much ~~en~~ energy
is used)

ruby: 27 pulses for 10 ns each
 \rightarrow power 0.2 GW

$\lambda = 694.3 \text{ nm}$ (red end of vis.)

very good monochromatic

very small beam divergence
coherent light

Nd-laser: also solid state

Nd^{3+} in $\text{Y}-\text{Al}-\cancel{\text{Fe}}-\text{garnet}$

\rightarrow YAG Laser

infrared $\lambda = 1064 \text{ nm}$

YAG Laser is a 4 level one

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with frequency doubling (laser)

→ 532 nm

green light

gas lasers : high powers

He/Ne laser

He is pumped by electric discharge
to 1S , 3S states

by collisions the excitation energy
goes into 3P metastable excited
states of Ne which give the
laser action.

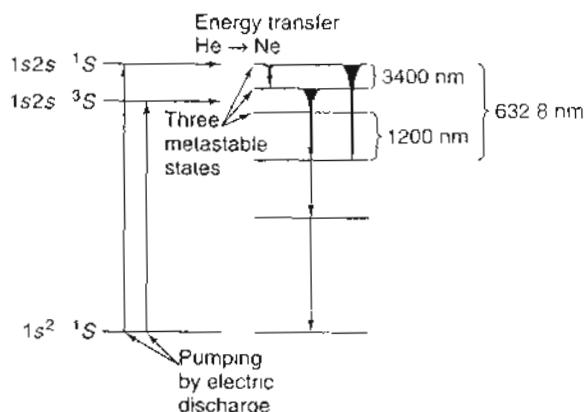


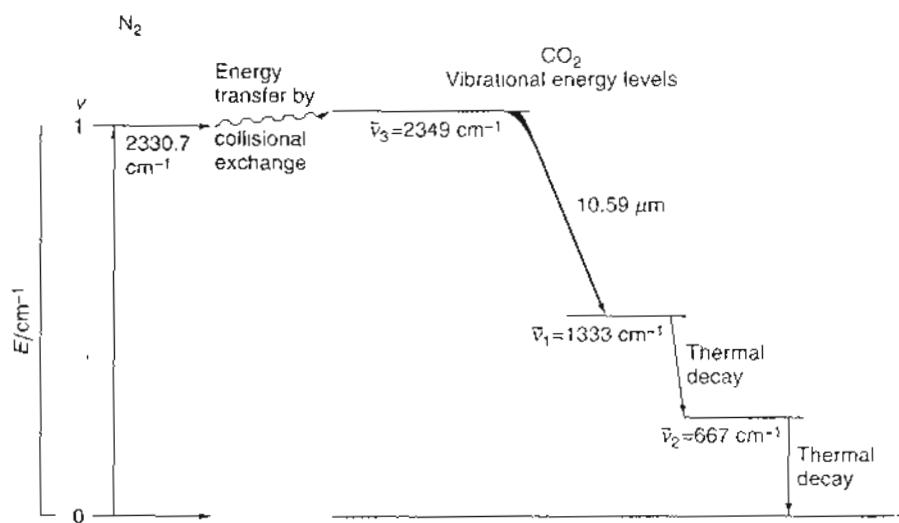
FIGURE 14.5
Energy levels in a helium-neon laser showing transitions resulting in population inversion in three metastable states.

The first chemical laser was constructed in 1965 by the American chemists J. V. V. Kasper and George Claude Pimentel (1922–1989). It was based on the reaction $H + Cl_2 \rightarrow HCl^+ + H$, in which the HCl is formed with a population inversion of vibrational states. The feasibility of using this reaction in a laser was suggested in 1961 by John Polanyi on the basis of his molecular dynamics studies (Section 9.11).

1 Torr. For argon, both Ar^+ and Ar^{2+} ions are formed in excited states. Laser action drops the electrons to a lower state, where the ions emit ultraviolet radiation at 72 nm and are then neutralized. Because of the large number of lower states, there are many wavelengths in the spectra, but the emission from Ar^+ primarily gives light of 488 nm (in the blue region) and 514 nm (in the green region). The krypton-ion laser gives a wider range of wavelengths, the most intense being at 647 nm (in the red region).

Another type of laser provides extremely high power in the beam. The chemical laser, in which a chemical reaction generates molecules already in an inverted population state seems very promising. Such lasers have been envisioned by the military for several applications. In the now "on hold" Strategic Defense Initiative, better known as SDI or "Star Wars," photolysis of F_2 forms F atoms which attack H_2 molecules, with the production of HF and H. The H in turn attacks F_2 to form vibrationally excited or "hot" HF molecules. These occur with inverted populations,

FIGURE 14.6
Energy levels in the CO_2 laser showing transitions leading to energy transfer from N_2 to CO_2 with the resultant laser action of CO_2 .



CO_2 Laser

N_2 is excited by discharge
energy passes through collisions
and e-exchanges
into the antisymmetric stretching
vibration (ν_3) of CO_2

Laser action: $\nu_3 \rightarrow \nu_1$ (symm. stretch)

$$\lambda = 10.59 \mu\text{m}$$

Same principle: Ar, Kr lasers
discharge through the gases at
 ≈ 1 Torr pressure

Ar^+ , Ar^{2+} are formed (Ar Laser)

Laser action from a metastable
state of the ions

many lower states \rightarrow many wavelengths

Ar^+ mostly 488 nm (blue)

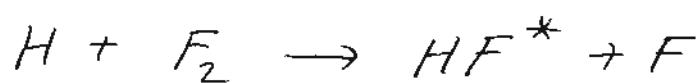
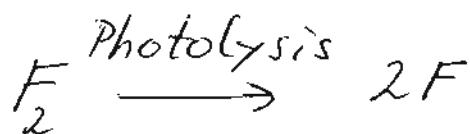
and 514 nm (green)

Kr: wider range, mostly 647 nm (red)

Chemical Lasers

Chemical reaction that yields products in excited states

→ population inversion



↳ excited

Excimer Lasers

Excimer: two atoms that can be bound in an excited state but not in groundstate

emission → ground state



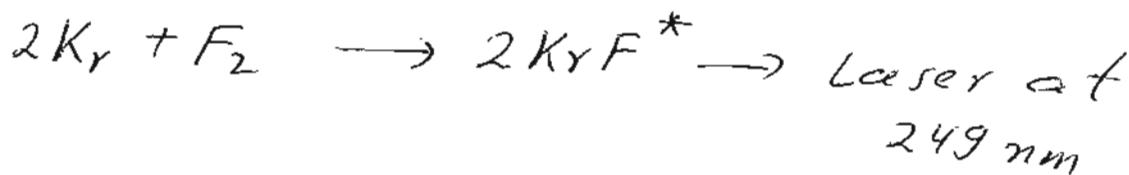
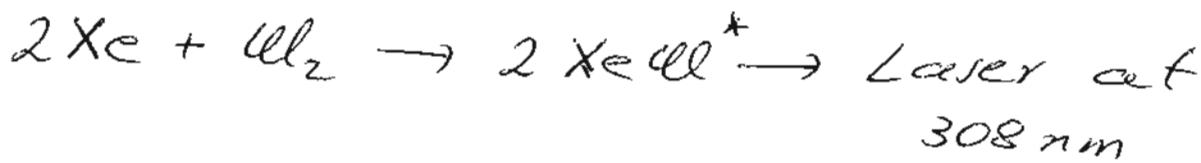
dissociation

→ population inversion

(no groundstate excimers exist)

again discharge through
gas mixtures

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both in Ne carrier gas

excimer life times $\approx 10\text{ ns}$

Frequency doubling

non linear effect

effect of light of normal intensity
on an atom in a crystal:

→ induced polarization P

$$P = \beta_1 E \xrightarrow{\text{optical}} \text{electric field}$$

β_1
polarizability

But if the light has high Intensity:

$$P = \beta_1 E + \beta_2 E^2 + \beta_3 E^3 + \dots$$

β_2, β_3
nonlinear

E_0 : amplitude of the radiation field in the crystal (light) (35)-11

$$E = E_0 \sin 2\pi\nu_0 t \text{ light}$$

→ nonlinear part of $P: P^{NL}$

$$P^{NL} = \beta_2 \cdot E_0^2 \sin^2 2\pi\nu_0 t$$

$$= \frac{1}{2} \beta_2 E_0^2 (1 - \cos 4\pi\nu_0 t)$$

→ two components are created:

a DC-field

and a double frequency oscillation

→ frequency doubling

≡ optical second harmonic generation

small Intensity: nonlinear effects too small to observe

→ used to for:

laser light → UV, X-ray Laser
occurs only in crystals without inversion center

example: piezoelectric crystals

different electrical properties
in different directions

obj Applications

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Line-widths

Applications

- Intensity of fluorescence can be increased
- Raman spectroscopy with Lasers
 - much better intensities than with arc-lamps
- monochromatic light
 - 0.1 cm^{-1} resolution
- stimulated Raman spectroscopy:
more quanta than 1 at a time
are given to or taken from
the sample → more lines:
 $\nu_0 \pm 2\nu_m, \nu_0 \pm 3\nu_m$
- resonance Raman spectroscopy
measured directly at the absorption frequency of the material

Coherent anti-Stokes Raman (36)-2

spectroscopy

study of species in flames

2 Laser beams ν_1, ν_2 are crossed
when passing the sample

→ combination frequencies

1 combined frequency is at

$$\nu' = 2\nu_1 - \nu_2$$

anti-Stokes line $\nu'' = \nu_1 + \nu_m$
 \uparrow
exciting \uparrow
sample
frequency

$\nu'' > \nu_1$ (exciting line)

anti-Stokes scattering

Variation of ν_2 such that

$$\begin{aligned} \nu_1 - \nu_2 &= \nu_m \\ \nu' = 2\nu_1 - \nu_2 &= \underbrace{\nu_1 - \nu_2}_{\nu_m} + \nu_1 \\ &= \nu_1 + \nu_m \\ &= \nu'' \quad \Rightarrow \quad \nu' = \nu'' \end{aligned}$$

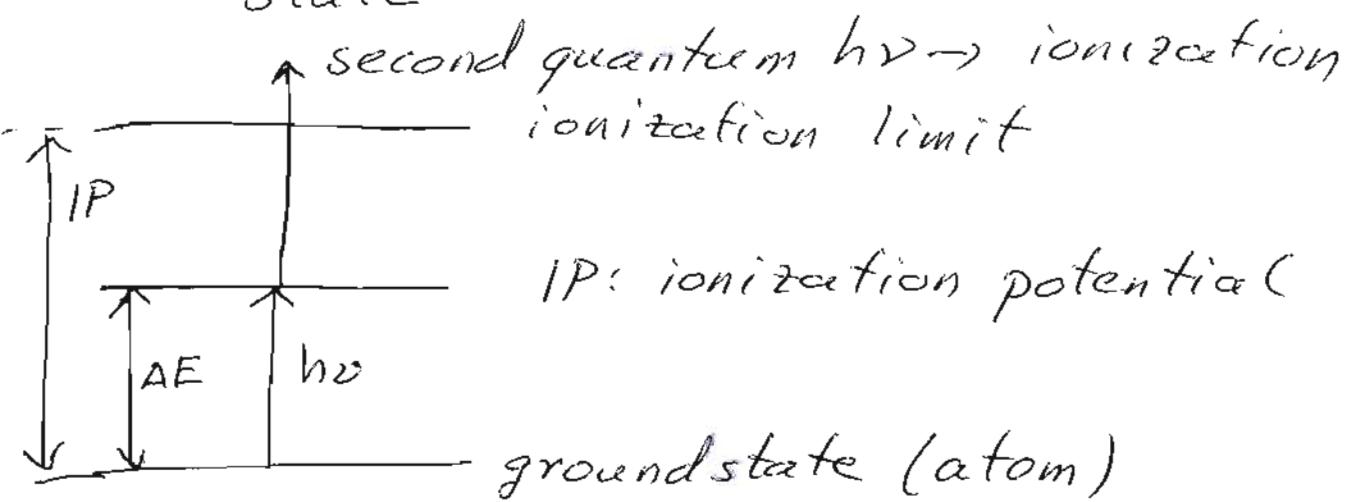
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then: ν' stimulates the emission
of the anti-Stokes line ν''
 \rightarrow higher intensity

Resonance ionization spectroscopy

Wavelength-tunable Laser

\rightarrow excitation of groundstate
electrons in atoms or molecules
to a precisely defined excited
state



\rightarrow excited state chosen such
that $IP \leq 2h\nu$

resonance process only, when
 $h\nu = \Delta E$ and $IP \leq 2h\nu$

→ Identification of all atoms (36)-4
in the periodic table possible
also precise photochemistry studies
exactly 1 vibration can be
excited and its influence on the
rate of reaction can be studied

Spectral line widths

transition → lines which are spread
over a range of
frequencies

2 fundamental reasons for line
broadening:

Doppler broadening

shift of wavelength to the red
if the emitting object moves away
from the observer

shift of λ to the blue if (36)-5
the emitting object moves towards
the observer

object with speed u that emits
light of wavelength λ , frequency ν
then the observer sees

$[1 - \frac{u}{c}] \nu$ red shift, if the object
moves away from observer

$[1 + \frac{u}{c}] \nu$ blue shift, if the object
moves towards observer

molecules in a gas move with many
different speeds in all directions

→ Doppler effect leads to many
 λ -values in a Maxwell
distribution

→ Gaussian line shape
bell shape

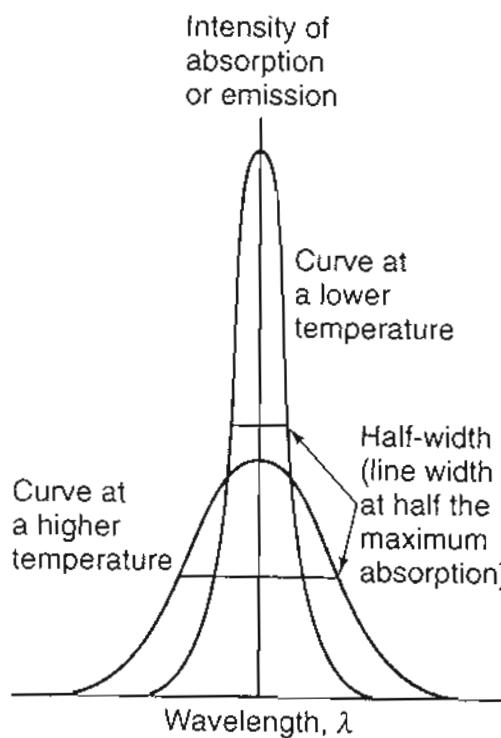


FIGURE 14.7
Line widths at two different temperatures as determined by the Gaussian distribution.

temperature rises. (Further discussion of this is given in Section 14.10.) The half-height of an absorption line may be found from

$$\Delta\lambda = 2\left(\frac{\lambda}{c}\right)(2k_B T/m)^{1/2}$$

where m is the mass of the species involved in the transition. To obtain the best resolution of spectral lines, the spectra should be taken at low temperature. High temperatures (such as the temperature of the sun) can be studied by measuring the broadening of a particular spectral line (see Figure 14.8).

Lifetime Broadening

A second mechanism which is important even at very low temperatures is a mechanical effect called *lifetime broadening*. Because of the finite lifetime of an excited state, it is impossible to specify exactly the energies of the states. Only if the state has an infinite lifetime can its energy be precisely defined. In reality, since no excited state has an infinite lifetime, no excited state has a precisely defined energy. The shorter the lifetime of an excited state, the broader the spectral lines.

The uncertainty principle may be used to estimate the expected width of a spectral line. From Eq. 11.64,

$$\Delta E \Delta \tau \approx \frac{\hbar}{4\pi} = \hbar/2 \quad (\hbar = h/2\pi)$$

The energy spread ΔE is therefore inversely proportional to the lifetime $\Delta \tau$. It follows that the corresponding broadening of the line is

$$\Delta\bar{v}/\text{cm}^{-1} \approx \frac{2.7 \times 10^{-12}}{\Delta\tau/\text{s}}$$

The radiative lifetime of an electronically excited species may be as short as 10^{-8} s, which leads to a line width of $\approx 2.7 \times 10^{-5} \text{ cm}^{-1}$. When an excited state undergoes dissociation or internal conversion, however, the lifetime may be as long as 10^{-10} s. This value gives a broadening of about 0.27 cm^{-1} , which can easily be detected.

form (~~height~~ width) depends on T

The larger T , the more α -values

→ the more λ values

width $\Delta\lambda$ at half-height

(half width):

$$\Delta\lambda = 2 \left(\frac{\lambda}{c} \right) \sqrt{\frac{2k_B T}{m}}$$

→ highest resolution at lowest possible temperature

Doppler line widths

→ temperature, e.g. on the sun

emission comes from the sun at

677.4 nm due to ionized ^{57}Fe

atoms with molar mass 56.94 g/mol

with a line width of 0.053 nm.

What is T on the sun (surface)

$$m = 56.94 \cdot 10^{-3} \frac{\text{kg}}{\text{mol} \cdot N_A} = 9.455 \cdot 10^{-26} \text{ kg}$$

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$$T = \left[\frac{1}{2} \frac{c \alpha \lambda}{\lambda} \right]^2 \cdot \frac{m}{2k_B} \\ = \left[\frac{0.053 \cdot 10^{-9} m \cdot 2.998 \cdot 10^8 \frac{m}{s}}{2 \cdot 677.4 \cdot 10^{-9} m} \right]^2 \cdot \\ \cdot \left[\frac{9.455 \cdot 10^{-26} \frac{kg}{J}}{2 \cdot 1.381 \cdot 10^{-23} \frac{J}{K}} \right]$$

$$= [1.172 \cdot 10^4]^2 \cdot 3.423 \cdot 10^{-3} K = 4.7 \cdot 10^5 K$$

($\Rightarrow {}^{57}\text{Fe}$ emits not on surface because there $T \approx 6000 \text{ K}$)

Life-time ~~broad~~ broadening

quantum effect at any T

based on Heisenberg's uncertainty principle

→ it is impossible to give the exact energy in a transition

only if the life-times of states is infinite, is the energy exact

all excited states have limited (36)-8 life-times

→ no precise energy can be measured

→ The shorter the life-time, the broader are the lines

$$\Delta E \cdot \Delta t \approx \frac{\hbar}{2} = \frac{\hbar}{4\pi}$$

$$\Delta E \approx \frac{\hbar}{2} \cdot \frac{1}{\Delta \tau}$$

$$\rightarrow \Delta \bar{\nu} (\text{cm}^{-1}) = \frac{\Delta E}{hc} = \frac{2.7 \cdot 10^{-12} \text{ cm}^{-1}}{\Delta \tau / \text{s}}$$

life-times of electronically excited states can be 10^{-7} s typically

→ line-width $\approx 2.7 \cdot 10^{-5} \text{ cm}^{-1}$

but life-times as low as 10^{-11} s or even further exist

in internal conversion or dissociation processes such life-times occur

→ broadening of $\approx 0.27 \text{ cm}^{-1}$

can easily be observed

EPR, NMR will ~~be~~ not be covered (not enough time)

magnetic resonance EPR (37)-1

and NMR we cancel. Too much
for time we have

Obj Mössbauer Spectroscopy

Photoelectron Spect.

Photo acoustic Spect.

Mössbauer Spect.

based on emission of γ -rays from
excited nuclei

usually very broad lines (large
 $\Delta\nu$) due to recoil (γ quanta
are of high energy)

recoil speed $\frac{N^*}{c}$ γ -quantum, ν
momentum

of recoil: $m\mu$ of photon $\frac{h\nu}{c}$

momentum conservation:

$$\frac{h\nu}{c} = m\mu$$

nucleus free in space to

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move: v (speed) large

→ Doppler broadening!

Mössbauer spectra:

N bound and fixed in crystal

→ m is then the much larger,
mass of the whole crystal

⇒ v small ⇒ $\Delta\nu$ very small

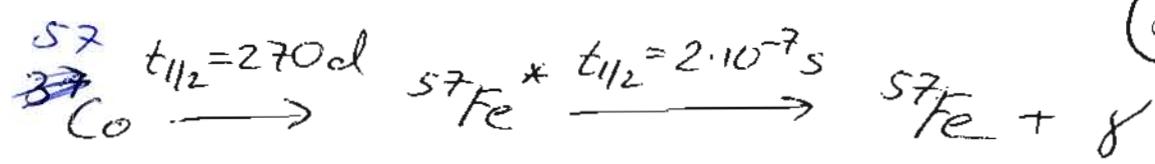
$\Delta\nu$ as small as 1 part in 10^{13}

→ test of Einstein's theory of
relativity and spectroscopy

source: ^{57}Co nucleus is unstable
half life 270 d

decays slowly to $^{57}\text{Fe}^*$

$^{57}\text{Fe}^*$ emits γ rays with a
half-life of $2 \cdot 10^{-7}$ s



$$\nu_\gamma = 3.5 \cdot 10^{18} \text{ Hz}$$

$$\rightarrow \text{energy } h\nu_\gamma = 2.32 \cdot 10^{-15} \text{ J} \\ = 14.5 \text{ keV}$$

life-time broadening of ν_γ : $\Delta\nu$

$$h \cdot \Delta\nu = \Delta E$$

$$\Delta E \cdot \Delta t = h \Delta\nu \cdot t_{1/2} = \frac{\hbar}{2} (\geq \frac{\hbar}{2})$$

smallest value, $\frac{\hbar}{2}$, taken

$$\rightarrow \Delta\nu = \frac{h}{4\pi} \cdot \frac{1}{ht_{1/2}} = \frac{1}{4\pi t_{1/2}}$$

$$\Delta\nu = \frac{1}{4\pi \cdot 2 \cdot 10^{-7} \text{ s}} \approx 4 \cdot 10^5 \text{ Hz}$$

$$\rightarrow \frac{\Delta\nu}{\nu} = \frac{4 \cdot 10^5}{3.5 \cdot 10^{18}} \approx 10^{-13}$$

\Rightarrow very sharp line!

recoil of a free nucleus:

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larger $\Delta\nu$

Mössbauer's idea for spectroscopy:

fix the ^{57}Fe nuclei rigidly in a crystal

$\Delta\nu$ for free ^{57}Fe nucleus and for
lg of crystal in which ^{57}Fe is fixed

$$\text{recoil } m u = \frac{h\nu}{c} \text{ (photon momentum)}$$

$$h\nu = 2.32 \cdot 10^{-15} \text{ J}$$

a) free ^{57}Fe atom

$$\text{mass } m = 57 \cdot 10^{-3} \text{ kg} / 6.022 \cdot 10^{23}$$

$$= 9.47 \cdot 10^{-26} \text{ kg}$$

→ recoil speed:

$$u = \frac{h\nu}{cm}$$

$$= \frac{2.32 \cdot 10^{-15} \text{ J}}{2.998 \cdot 10^8 \frac{\text{m}}{\text{s}} \cdot 9.47 \cdot 10^{-26} \text{ kg}} \cancel{\text{J}}$$

$$= 81.7 \frac{\text{m}}{\text{s}}$$

Doppler effect:

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$$\nu' = \left[1 + \frac{u}{c}\right] \nu$$

$$\frac{\Delta\nu}{\nu} = \frac{u}{c}$$

$$\nu' - \nu = \Delta\nu = \frac{u}{c} \nu$$

$$\frac{\Delta\nu}{\nu} = \frac{u}{c}$$

$$\rightarrow \Delta\nu = \frac{u}{c} \nu = 9.5 \cdot 10^{11} \text{ Hz}$$

$$\rightarrow \Delta\nu_{\text{Doppler}} \gg \Delta\nu_{\text{life-time}}$$

b) ^{57}Fe in Ig crystal:

$$m = 1g \rightarrow u = 7.74 \cdot 10^{-21} \frac{m}{s}$$

$$\rightarrow \Delta\nu = 9.04 \cdot 10^{11} \text{ Hz}$$

$$\Delta\nu_{t_{1/2}} = 4 \cdot 10^5 \text{ Hz}$$

$$\rightarrow \Delta\nu_{\text{Doppler}} \ll \Delta\nu_{\text{life-time}}$$

when ^{57}Fe is fixed in a Ig crystal

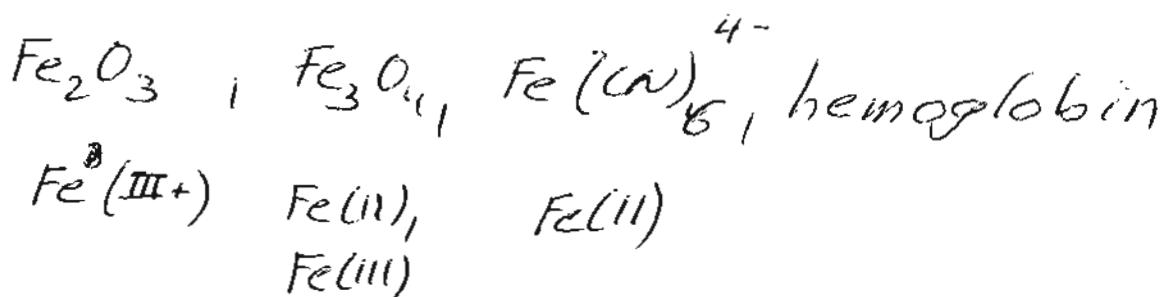
\Rightarrow very sharp line

spectroscopy

in a sample ν can be absorbed
e.g. by another ^{57}Fe nucleus

and the absorption observed

However: the absorption depends
on the valence state of
the Fe:



Differences up to 100 MHz in
absorption frequency, depending
on chemical surrounding

$$100 \text{ MHz} \ll \gamma_f \quad \underline{\text{but}} \quad 100 \text{ MHz} \gg \Delta\nu_{\text{eff}}$$

→ measurable!

needed is:

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control of γ frequency

→ use of Doppler effect

Source moves with exact speed
on a slider towards or away
from the sample

→ variation in γ

→ absorption spectrum can be
measured

100 MHz → speeds small

$$u = 5 \frac{\text{mm}}{\text{s}} \rightarrow \nu_{\gamma}^2$$

Doppler shift: $\Delta\nu = \frac{u}{c} \cdot \nu_0$

$$= 5.84 \cdot 10^7 \text{ Hz}$$

$$= 58.4 \text{ MHz}$$

→ when u only $5 \frac{\text{mm}}{\text{s}}$, ν_{γ} is
changed by 58.4 MHz

Photo electron spectrosc. (37)-8

PES

Einstein explained that in the development of quantum theory

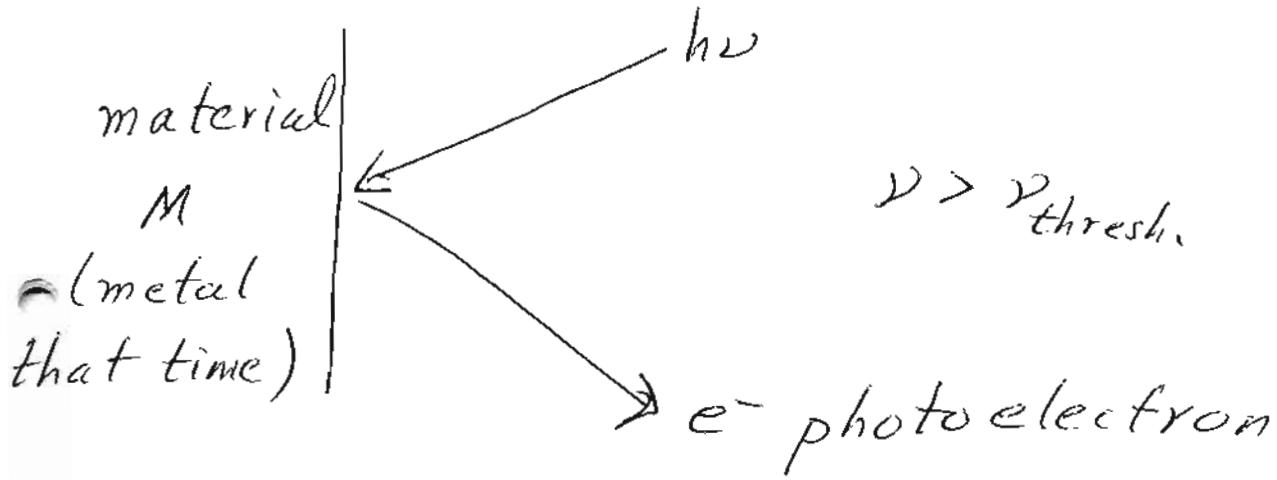
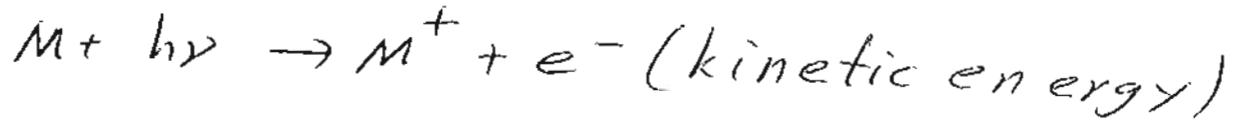


Photo electron spectrosc.:

measurement of kinetic energy of the emitted electrons



$$E_k(e^-) = h\nu - h\nu_{thrs}$$

in PES : usually UV source

He discharge lamp

→ 58.4 nm UV light (21.2 eV)

if $h\nu$ not enough for

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• $h\nu_{\text{thrs}}$ of a sample or for ionization

of core states deep in the atoms

→ larger energy needed

→ X-rays: XPS instead of PES

in the above reaction energy
must be conserved

E_k = kinetic energy of emitted e^-

$$E(M) + h\nu = E(M^+) + E_k (e^-)$$

$$E(M^+) - E(M) = \underbrace{h\nu - E_k}_{\text{ionization energy of the molecule } M}$$

$h\nu$ from the source is known

E_k is measured

→ ionization energies of the e^-
in molecules M

spectrum

plot of rate of e^- - emission ($\frac{\text{counts}}{\text{s}}$)
vs. $E_k(e^-)$

or vs. ionization energy $I = h\nu - E_k(e^-)$

 N_2 spectrum (later)

Source: 58.4 nm $\approx 21.2 \text{ eV}$

\Rightarrow sum of the 2 energy scale
(upper: photo electron energy in eV
lower*: ionization energy in eV)

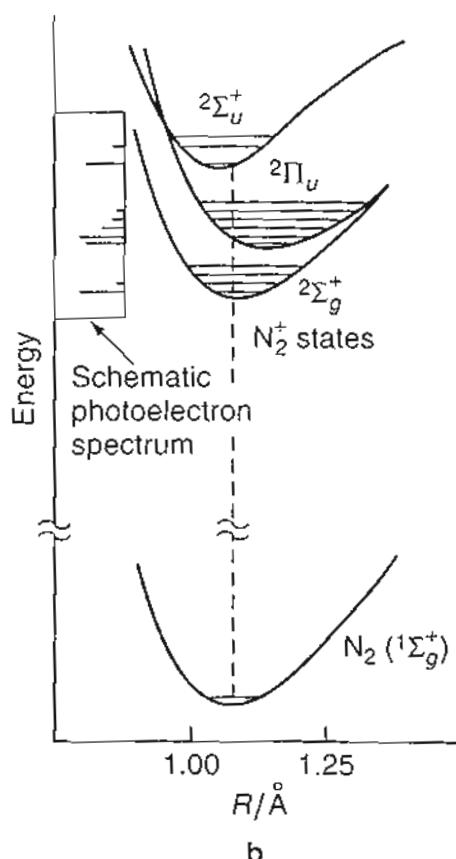
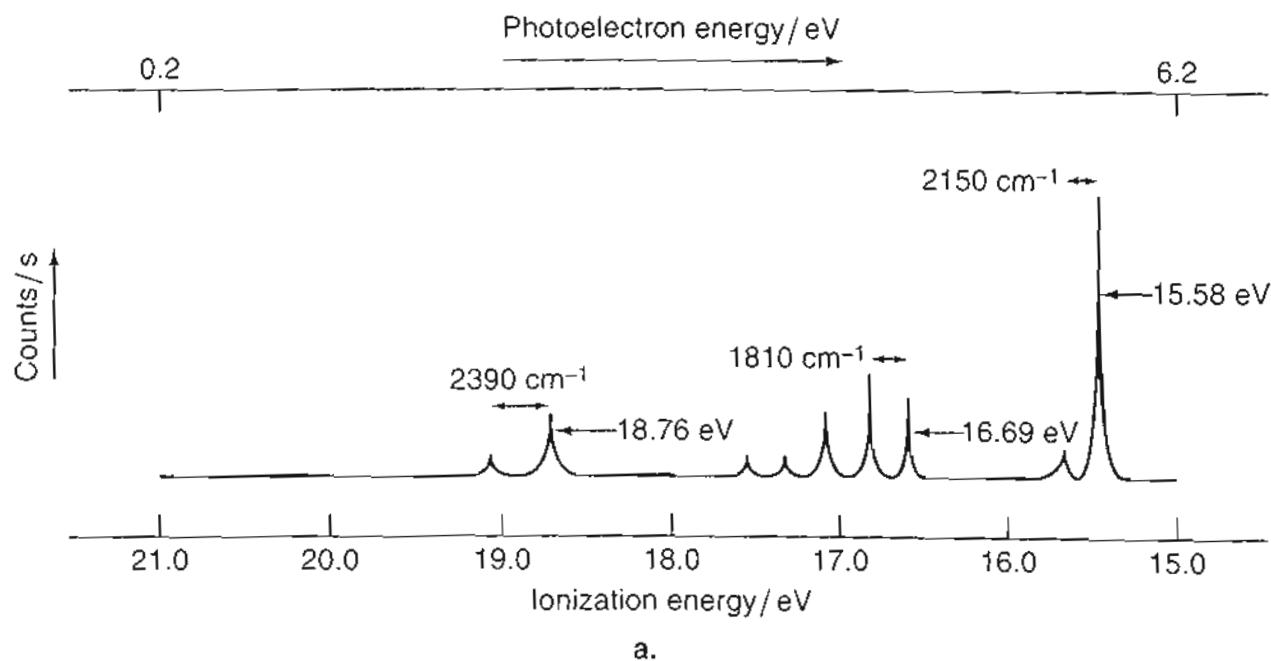
* I must be 21.2 eV in each point

3 groups of lines in N_2 ~~spectrum~~
from ionization of e^- from different
electronic levels

individual lines in a group:
vibrational levels
(fine structure)

TRON SPECTROSCOPY

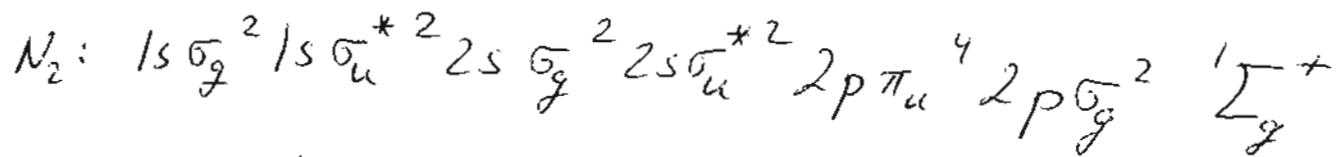
The importance of the photoelectric effect in the development of quantum theory was discussed in Section 11.1. Photoelectron spectroscopy (PES) measures the kinetic



(37)-11

Frank-Condon principle:

vertical transitions to the different excited states

(in PES 1 e^- is lost in N_2 \rightarrow excited state of N_2^+)

only $v=0$ thermally occupied
first 2 line, 15.88 eV

electron freed from $2p\sigma_g^2$ orbital $\rightarrow N_2^+ \text{ in } ^2\Sigma_g^+$

$(v'=0 \leftarrow v''=0 \text{ here and a small}$
 $N_2^+ \qquad N_2$

 $\text{or } v'=1 \leftarrow v''=0 \text{ (Frank-Condon))}$ next set starts at 16.69 eV $2p\pi_u$ electron is set free of N_2 $\rightarrow N_2^+ 2\pi_u$ many v' possible and vertical
final set: removal from $2s\sigma_u^* e^-$ $\rightarrow N_2^+ 2\Sigma_u^+$

in XPS: individual atoms in
different states can be
identified

(37)-12

reason: innermost $1s e^-$ different in
different elements and chemical
environments

Spectrum: $1s$ XPS spectrum of
ethyl chloro formate
shifts of XPS C- $1s$ lines for
different C atoms C_1, C_2, C_3
→ information on chemical structures
and bonding

right peak: $4l-2s e^-$

Section on mass spectroscopy
too short and not well written,
so we cancel that.

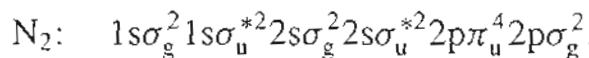
Information is gained from the process in Eq. 14 conservation of energy:

$$E(M^+) - E(M) = h\nu - E(e^-)$$

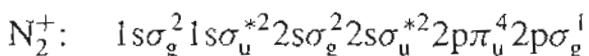
where $E(M)$ and $E(M^+)$ are the energies of the molecule by the ionization, and $E(e^-)$ is the kinetic energy of the known and $E(e^-)$ is measured, the difference between the original molecule is obtained.

Either of two plots gives the photoelectric spectrum electron emission against the electron kinetic energy; the emission against ionization energy (the right-hand side shows the spectrum for nitrogen with two energy scales and the ionization energy. Note that since the 58.4-nm 21.2 eV, the sum of the two scales is 21.2 eV at any point the figure correspond to ionization from three different lines in each group being the vibrational levels. Figure electron occupancy as deduced from the photoelectron is an electron transition to excited electronic states, this applies. But notice that the occupancy (as indicated by the 1 vibrational states, especially in the ${}^2\Pi_u$ state, corresponds of finding the electron near the end-most positions for a levels of the harmonic oscillator curve.

Because the sample is at room temperature, only the significantly occupied. From Section 12.5, the configuration is



The 2 lines starting at 15.88 eV correspond to the removal of an electron. The resulting state is



Going to the left, the next set of lines beginning at 16.69 eV of a $2p\pi_u$ bonding electron. The final excited state corresponds to an antibonding electron.

As indicated earlier, these techniques are not limited to molecules. However, when more energy is required to examine inner shell electrons, the energy differences between 1s levels for C, O, S, individual elements are easily identified by their energy differences in the carbon 1s spectrum, etc. In Figure 14.18 the carbon 1s X-ray

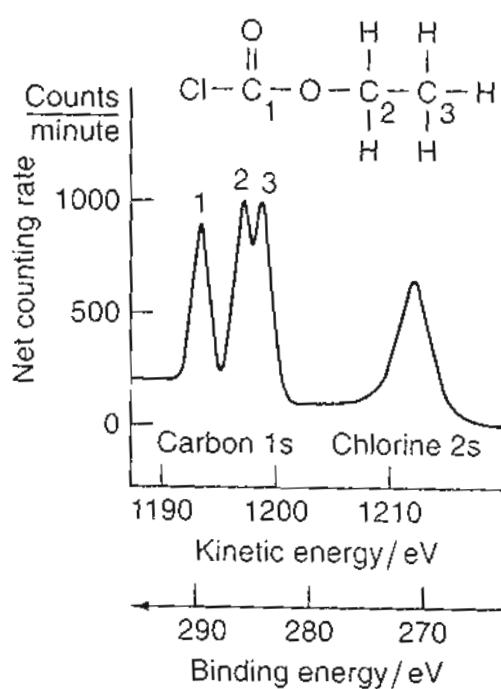


FIGURE 14.18

Photoelectron spectrum of ethyl chloroformate. The three lines in the carbon 1s spectrum appear in the same order from left to right as the carbon atoms drawn in the structure. (From: James, T. L., *Journal of Chemical Education*, Vol. 48, pp. 712–718, 1971. Used with permission.)

Photoacoustic spectros.

(37)-13

Monochromatic radiation pulses hit the material in the sample can be absorbed by sample or not (depending on radiation ν) ~~or~~ during pulse time

if absorption: the surface and the air around it are heated in pulse time

if outside pulse time: interrupt of heating \rightarrow air cools

air expands when heated, contracts when cooled \rightarrow sound wave emitted

if pulses and interrupts are long enough for heating and cooling

a sound is measured with microphone

spectrum: sound intensity vs ν

good for opaque materials and strongly absorbing substances

Chiroptical Methods

(38)-1

based on behavior of plane of polarized light when interacting with a chiral center

Nature of polarized light

electromagn. radiation: $\vec{E} \perp \vec{B} \perp \vec{v}$

normal light: \vec{E} vector points into all directions $\perp \vec{v}$ and so does \vec{B}

circularly polarized light

\vec{E} rotates around \vec{v} axis

the rotation can go to the left (L) or to the right (R)

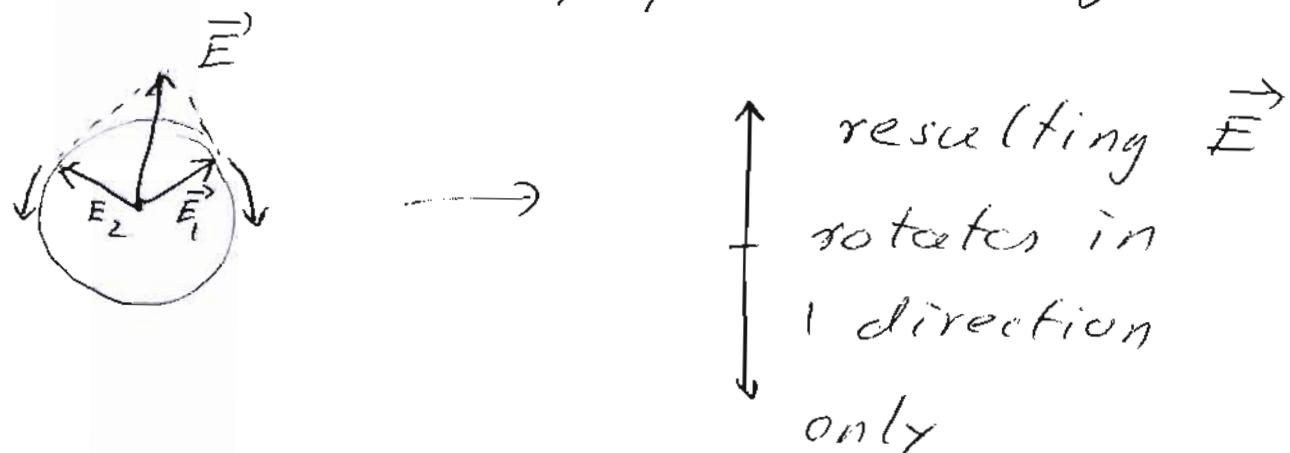
2 beams like that moving together:
equal rotation speeds of \vec{E} , but
1 wave is left, the other one
right circularly polarized

result of vector addition (38)-2

of the two \vec{E} field vectors:

\vec{E} oscillating in 1 direction only:

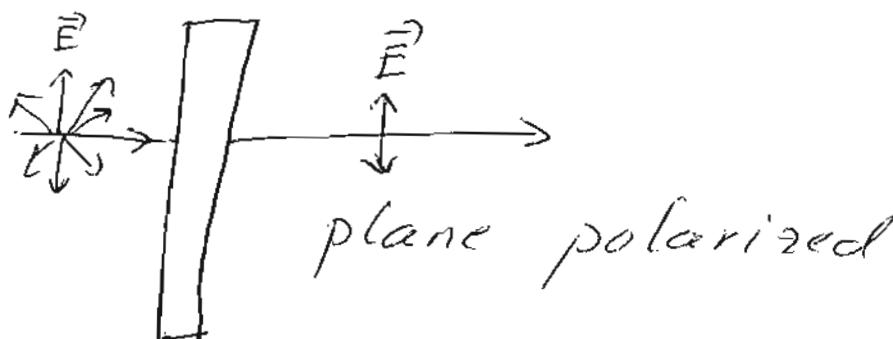
plane or linearly polarized light



how to create?

- 1) selective absorption by a dichroic material: material that allows only 1 \vec{E} direction to pass through it

Light with any other \vec{E} direction is absorbed



e.g. Poly vinyl alcohol,

(38)-3

aligned

it conducts along the conjugated chain direction

→ all light with \vec{E} that has any component along the chain direction can be absorbed

only light with $\vec{E} \perp$ chains

is not absorbed

→ aligned material lets only 1 \vec{E} direction \perp chains through
→ polarized light

2) reflected light is, mostly partially, polarized

if light ^{hits a mirror} ~~is reflected~~ along 0°

or 90° to the mirror no polarization

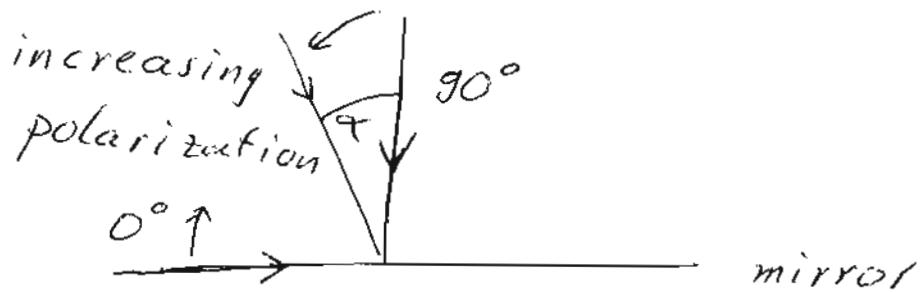
~~incident~~ reflected light at angle α (38)-4

shows increasing polarization
in reflection,
when α moves away from 0°
or 90°

~~incident~~ reflection angle α , where the
polarization is at maximum:

Brewster's angle = $f(\lambda)$

different for different α



reflection angle = incident angle

3) double refraction

amorphous material:

speed of light is the same in all
directions in the material

glas e.g.

in ~~single~~ crystals like

(38)-5

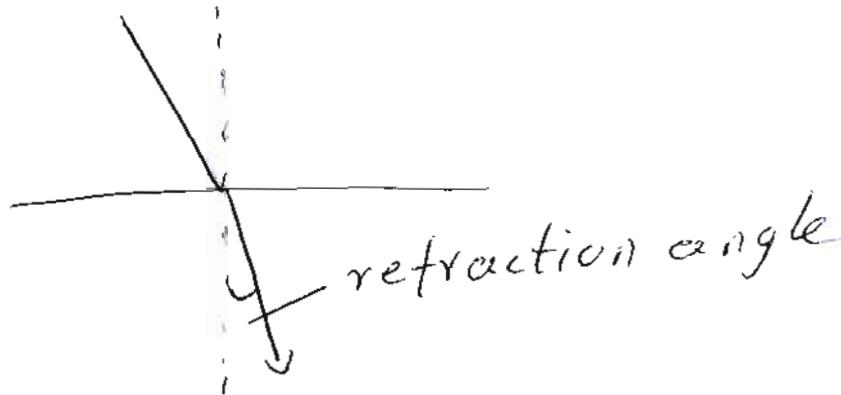
calcite (Na_2CO_3)

NaNO_3 :

~~→~~ 2 different speeds of light,
depending on the direction

→ 2 different refraction indices

when one look through calcite
on a black line behind it,
one sees the line double,
because of the 2 different
refraction angles



refraction angle = reflection angle
in birefringent or double refracting
materials: both beams are
polarized \perp to each other

4) scattering:

(38)-6

absorption and re-emission of
light (e.g. Raman effect)

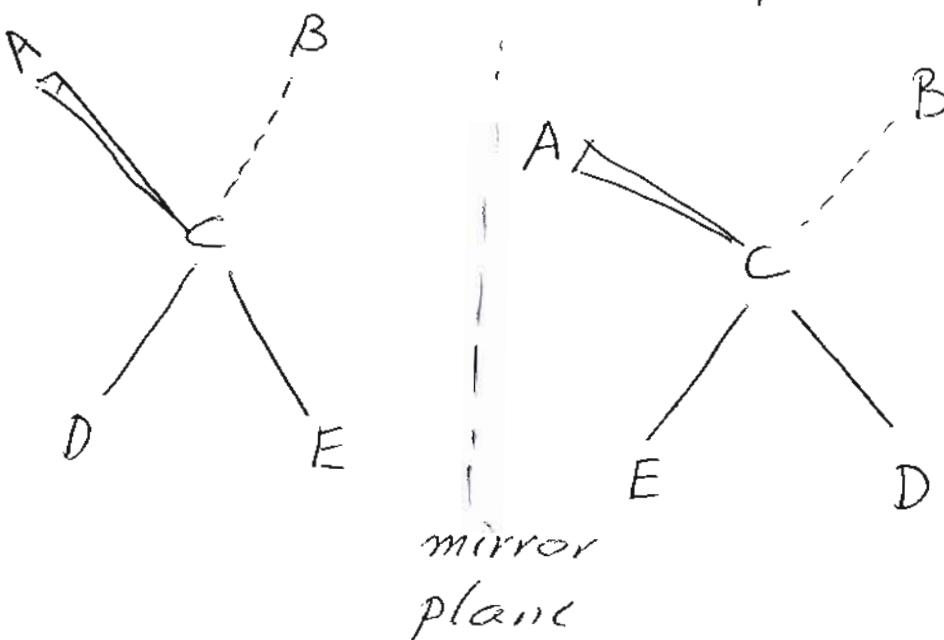
→ polarization

optical activity

the plane of polarized light becomes
rotated when passing a sample

e.g. asymmetric C atoms in a
molecule: C with 4 different
atoms bound to it (chiral)

chiral: mirror image of molecule
different from original



in nature only 1 type of 38 - 7

chiral amino acids appears

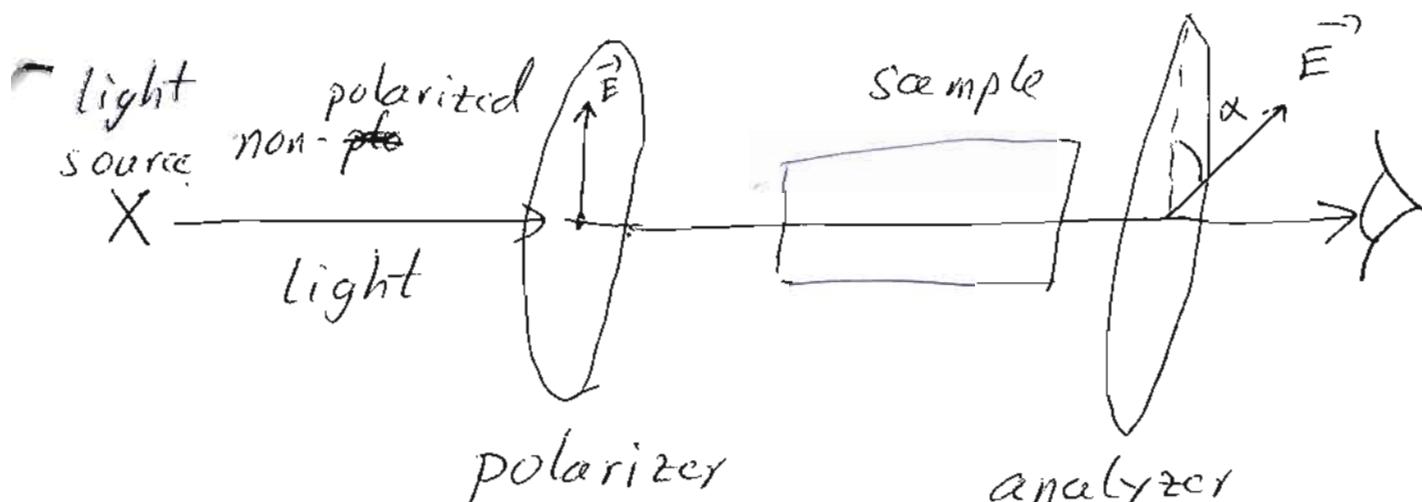
if a molecule has an inversion center
or a symmetry plane:

no optical ~~affinity~~ activity

optical activity can also result
from crystal symmetry

Quartz e.g. contains spirals and is
optically active (crystals)

molten quartz is not



e.g. Nicol prisms

cut e.g. a calcite crystal (38)-8

in half along a crystal axis

glue the halves rotated together

then the interface can be passed
only by one polarization direction

other components suffer total reflection
polarizer and analyzer can both
be Nicol prisms

at a given λ maximum transmission
angle of the prisms are measured
with and without sample

difference: angle of rotation α
the angle can be positive (sample
is dextrorotatory), if analyzer
must be turned to the right to
get maximum transmission, as seen
by the observer.

(38)-9

or the sample can be

laevo rotatory, & negative, if a left turn is needed

chiral centers interact with the right and left circular components of polarized light, like they have 2 refractive indices: n_L, n_R

$$\text{optical rotation: } \alpha' = \frac{\pi}{\lambda} (n_L - n_R)$$

for visible light

→ large α' : rotation/meter light path

chemical reaction: mix equal mixtures of d and l enantiomers

→ no optical activity

an optically active sample (38) - 10

of concentration $0.110 \frac{g}{cm^3}$ ~~- 0.110 m~~

rotates polarized light of Na-D line at 589 nm by $+25.4^\circ$ when passed through a ~~at~~ 1.00 dm tube

$$n_L - n_R ?$$

$$\alpha = \frac{180^\circ}{\pi} \alpha' \cdot l = \frac{180^\circ}{\lambda} (n_L - n_R) l$$

$$n_L - n_R = \frac{\alpha l}{l \cdot 180^\circ} = \frac{25^\circ \cdot 589 \cdot 10^{-7} m}{0.100 m \cdot 180^\circ} = 8.31 \cdot 10^{-7}$$

experimental: rotation $\sim c$ and l

$$\rightarrow \text{specific rotation } [\alpha]_A = \frac{\alpha}{c \cdot l}$$

$$[\alpha]_A = \frac{25.4^\circ}{0.110 \frac{g}{cm^3} \cdot 10^{-3} \frac{kg}{g} \cdot 0.100 m \cdot 100 \frac{cm}{m}}$$

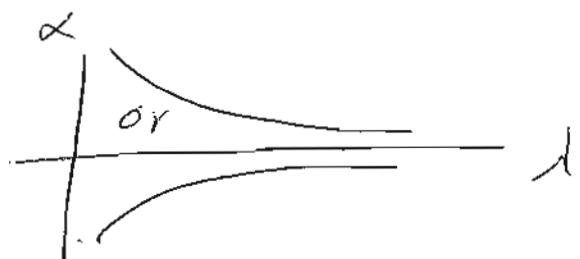
$$= 2.31^\circ \frac{m^2}{kg} = 2.31^\circ \frac{cm^3}{dm \cdot g}$$

Optical rotatory dispersion

(ORD)

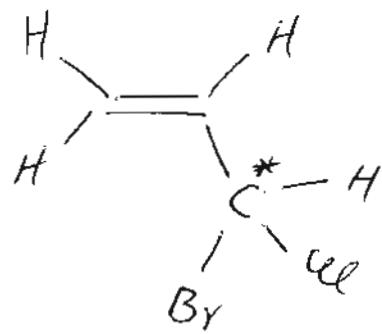
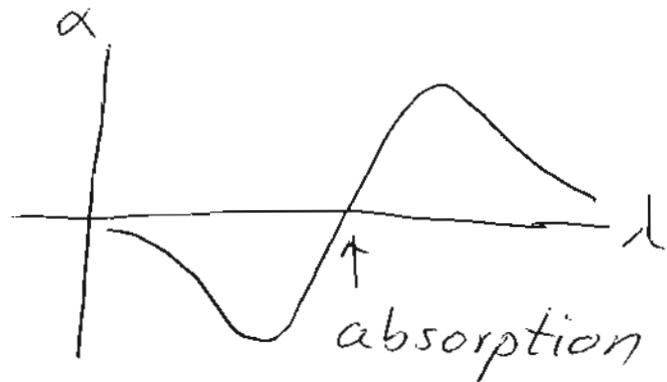
ORD spectrum without absorption

close to the chiral center



if any chromophor (absorbing group) bound to a chiral center:

Cotton effect:



multiple Cotton effects can appear

circular dichroism (CD)

(38)-12

different absorption of a chromophore for L or R circularly polarized light

R-beam can e.g. be stronger absorbed than L-beam
→ elliptically polarized light

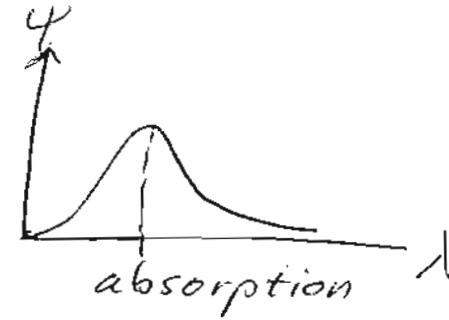
main axis lengths OA and OB

of the ellipse on which the \vec{E} vector rotates around \vec{V}

then ellipticity $\Psi = \arctan\left(\frac{OA}{OB}\right)$
if chiral center bound to the chromophor (rotation by α):

$$\Psi = \frac{\pi}{\lambda} (\varepsilon_L - \varepsilon_R)$$

molar absorption



CD effect only at λ of absorption

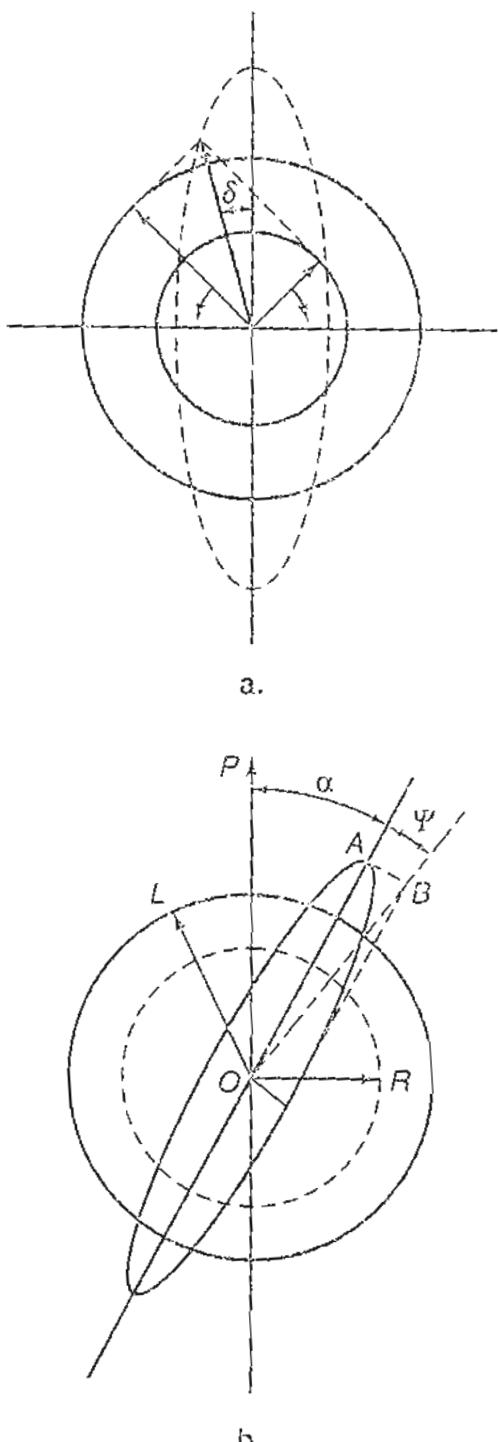


FIGURE 14.23

(a) The representation of elliptically polarized light arising from two circularly polarized beams having different extinction coefficients.
 (b) The representation of elliptically polarized light combining the effects of a difference in refractive index.

Optical Rotatory Dispersion (ORD)

Polarimetry and optical rotatory dispersion both measure of linearly polarized light is rotated by a chiral or helical sample, that is, for one without chromophores, both techniques with polarimetry limited to the wavelength of the excited absorption by a chromophore, the ORD spectrum is limited to the wavelength. See Figure 14.22a.

If the optically active center is adjacent to a chromophore in a polarized beam, anomalous rotations in the ORD spectrum in Figure 14.22b. This behavior, known as the *Cotton effect* (after physicist A. Cotton) is superimposed on the monotonic rotation is limited to the wavelength range of the absorption band or a changed sign minimum. See Section 20.6 for a further discussion.

Circular Dichroism (CD)

Circular dichroism is concerned with the change in the intensity of light with the differential absorption by the chromophore of left- and right-circularly polarized waves. Figure 14.22c shows a CD curve with a positive peak at λ_1 and a negative peak at λ_2 . Figure 14.23a shows how elliptically polarized light is generated by the combination of two circularly polarized beams. Figure 14.23b shows how the intensity of the right circularly polarized beam caused by the difference in refractive index of the two media. The effects are combined, as in Figure 14.23b, the long axis of the ellipse is defined by the angle α . The ellipticity is defined by $\Psi = \tan^{-1}(OA/OB)$. Ψ is called the ellipticity and is related to the absorbance difference,

$$\Psi = \pi(\epsilon_L - \epsilon_R)/\lambda$$

where ϵ is the molar absorptivity, the L and R standing for left and right circularly polarized light, and λ is the wavelength at which the ellipticity is maximum.

CD can have both positive and negative deviations from the value of zero. The advantage of CD over ORD is that there is no signal at wavelengths where the sample has no absorption; consequently, the baseline is easy to define. Circular dichroism has applications to the determination of conformations, and it is a technique which promises to become a major thrust in future years.

①

NMR

Nuclear Magnetic Resonance

radio frequencies (VHF band)

based on nuclear spins

ESR

Electron Spin Resonance

> 1 unpaired e^- in sample (NO)

EPR

Electron Paramagnetic Resonance

> 1 unpaired e^- in sample (O_2)

Zeeman splitting from an electron spin

≥ 1000 times that from nuclear spin

→ EPR in microwave region

both give very weak signals

two levels in magnetic fields (B)
external field

$$\Delta E \sim \nu$$

$$\Delta E \sim B$$

in EPR & NMR:

(2)

$\nu = \text{const.}$ radio or microwave frequency and

external field B slowly changed observed is absorption of $\nu = \text{const.}$

when B changes, resonance at B_0

when $\Delta E = h\nu$

weak signals: spectra recorded

many times and superimposed to minimize signal/noise

- pulse at $\nu = \text{const.}$ at some B value
measure absorption as $f(t)$

then Fourier transformation yields absorption as $f(\nu)$

relaxation back into equilibrium after the pulse

repeat for other B values

B is usually scanned through in
one run ③

strong $E = \text{const.}$ fields (starkfields)

not used too much

but $\underline{B} = \text{const.}$ laboratory fields

always applied

B -field of wave in x direction: $B_x^0 \underline{e}_x$
(amplitude)

$B = \text{const.}$ field in z direction: $B_0 \underline{e}_z$

\underline{e}_x unit vector in x direction

total: $\underline{B} = B_0 \underline{e}_z + B_x^0 \cos \omega t \underline{e}_x$

electric:

+ or -

monopoles



+
- - -
+ quadupoles

magnetic

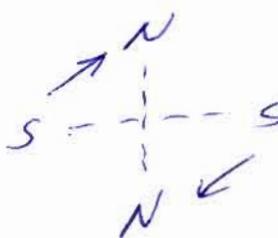
no monopoles

found so far

N north

S south

dipole



N S
quadrupole

static magnetic field B_0 (4)

μ_B Bohr's magneton = $9.274 \cdot 10^{-24} \frac{2}{T}$

g_s spin gyromagnetic ration

$1e^-$ in B_0 : Zeeman splitting

$$E_{\pm \frac{1}{2}} = \pm \frac{1}{2} g_s \mu_B B_0 \quad \text{two non-deg. levels}$$

ESR splitting

$$\text{Dipole: } \mu_N = \frac{e\hbar}{4\pi m_p} = 5.0508 \cdot 10^{-27} \frac{T}{T}$$

nuclear nuclei: spin \rightarrow NMR, g_s gyromagnetic ratio

$$^1H: \text{nuclear spin } \frac{1}{2} \quad g = 2.67 \cdot 10^8 \frac{\text{rad}}{T \text{s}}$$

$$^2H: \text{spin } 1 \quad g = 0.411 \frac{\text{rad}}{T \text{s}}$$

$$^{12}C: \text{spin } 0 \quad ^{13}C \text{ spin } \frac{1}{2}$$

$$^{15}N: \text{spin } \frac{1}{2} \quad ^{14}N \text{ spin } 1 \quad (\text{most common})$$
$$-0.271 \frac{\text{rad}}{T \text{s}} \quad 0.193 \frac{\text{rad}}{T \text{s}}$$

spin: I , multiplicity $2I+1$ degenerate levels when $B_0=0$

magn. moment operator for a nucleus i with spin I_i

$$\mu_i = g_i \hbar I_i$$

not only ~~spins~~ spins give magn. fields also rotating charges, i.e. \vec{J} in a diatomic or rot. electrons

$$\mu_J = g_J \hbar J \text{ (rotating } e^-)$$

(5)

J: 2J+1 levels

Different magnetic couplings

Zeeman effect

$$\hat{H}_I = -\hbar g_I (1-\sigma_i) I_z B_0$$

B₀ in z-direction
magn. moment of system

σ_i : chemical shielding (NMR)

shift of resonance frequency of I
with B (\hookrightarrow determined by σ_I only)

depending on chem. environment:

e⁻ density around I

Indirect ~~scalar~~ scalar spin-spin J-coupling

a spin yields a local magn. field
which can couple to other near spins

J₁₂ coupling constant (not J in rotors)

$$\hat{H}_{12}^{\text{J-coupl.}} = \hbar J_{12} \overset{\leftarrow}{I_1} \cdot \overset{\leftarrow}{I_2} \text{ scalar product}$$

\rightarrow multiplets in ~~#~~ NMR

Direct spin-spin coupling

⑥

\mathcal{J} -coupling: through bonds coupling



directs through space ($r < 5\text{\AA}$)
distance of spins

$$\hat{H}_{12}^{\text{direct spin-spin}} = \frac{\hbar \delta_1 \delta_2}{r^3} (3 \cos^2 \theta - 1) \cdot$$

$$\cdot [I_{1z} I_{2z} - \frac{1}{2} (I_{1x} I_{2y} + I_{1y} I_{2x})]$$

θ : ∇ (system, B_0)
main axis

causes broad lines in solid state NMR

→ removal by magic angle spinning

sample spins (high speed) with spinning axis to B_0 angle $\theta = 54.74^\circ$

$$\text{then : } (3 \cos^2 \theta_0 - 1) = 0$$

spin (1) - rotation (\mathcal{J}) coupling

$$\hat{H}_{1\mathcal{J}}^{\text{spin-rot}} = C_{\text{sr}} \underline{\frac{1}{2} \cdot \mathcal{J}}$$

small

Nuclear quadrupole interactions

(7)

nuclei $I > \frac{1}{2}$: quadrupole moments

non-isotropic E-field

→ energy of nucleus depends on orientation between spin and E-field gradient

→ determines orientation \perp to B_0

spin $\frac{1}{2}$: only 2 orientations with same energy in quadrupole field → levels degenerate

spin $I=1$: ± 1 levels degenerate but $I=0$ level different

→ additional line splittings for $I > \frac{1}{2}$ in non-isotropic E-field

Liquids: averaged out by motion of particles

but seen in solids

(8)

nuclear spin I :

$$\hat{H}_I^{\text{quadrupole}} = d_I [3I_z^2 - I(I+1)]$$

$$\hat{H}_J^{\text{quadrupole}} = d_J [3J_z^2 - J(J+1)]$$

• rotations

d_I, d_J quadrupole strengths

also seen centrifugal distortions:

diamagnetic effects due to vibrations

non-linear effects at large B_0 :

$$\hat{H}^{\text{nonlinear}} = f I^2 B_0^2$$

Diamagnetic samples:

small repulsions by B fields

Paramagnetic samples:

attractions by B fields

Ferromagnetic samples: (Fe)

ordered spin domains (FPI)

strong attractions by B fields

EPR

(9)

Continuous wave (CW) method:

microwave signal continuous

pulse method:

microwave signal pulsed

mostly CW experiments

EPR: less improvement by averaging
runs than in NMR
several reasons

ESR: 1 spin NO₂, radicals H, CH₃
(stable)

and α ions like C₆H₅⁻

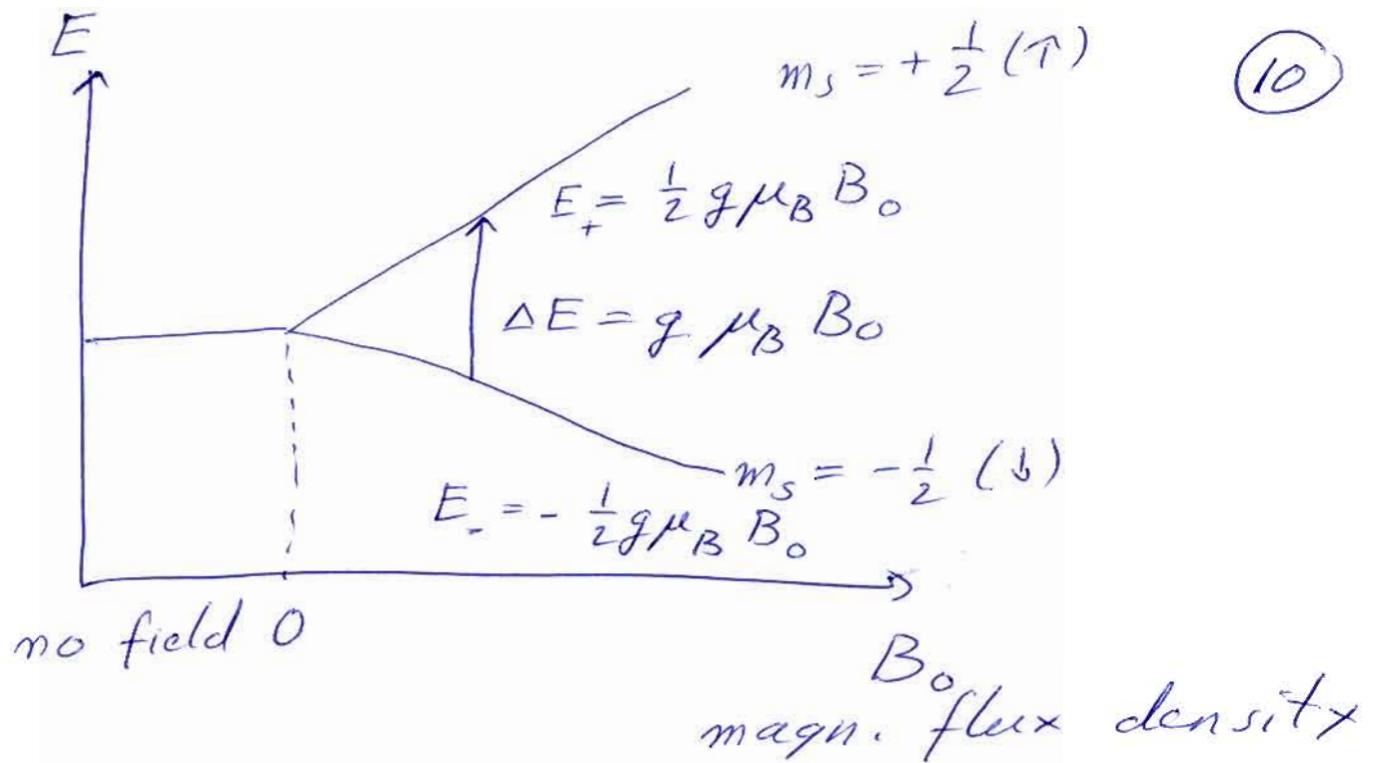
EPR > 1 spin, e.g. 2 in O₂

similar basic concepts as in NMR

1 electron in field B₀

$$\Delta E = h\nu = g \mu_B B_0$$

1
Lande g-factor (see Chap. 13)
from spin-orbit coupling



transition (abs) from $-m$ to $+m$

chemical shielding important and
hyperfine interaction:

electron spins + nuclear spins

multiplets similar to π -coupling
in NMR

EPR to liquids, powders,
single crystals

g -factors and hyperfine coupling
constants: usually anisotropic
tensors

$$\nu = 9,100 \text{ GHz}$$

(11)

in experiment with H atoms

Resonance: $B = 0,3247 \text{ T}$

$g = ?$ for e^- in H atom's

$$h\nu = g\mu_B B$$

$$\rightarrow g = \frac{h\nu}{\mu_B B}$$

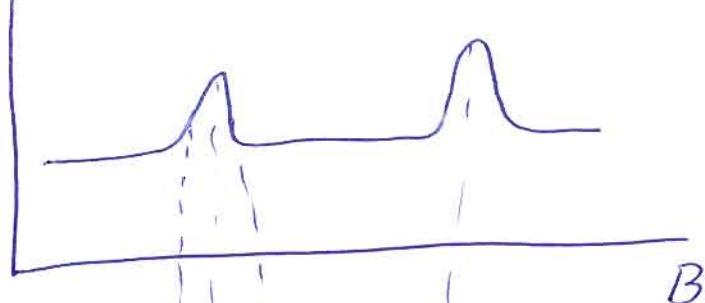
$$= \frac{6,626 \cdot 10^{-34} \text{ Js} \cdot 9,100 \cdot 10^9 \text{ s}^{-1}}{9,274 \cdot 10^{-24} \text{ T} \cdot 0,3247 \text{ T}}$$

$$= 2,0024$$

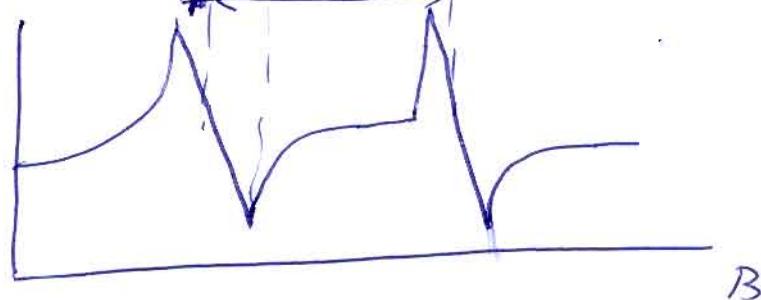
Hyperfine Structure

e.g. 2 peak because e^- -spin - nucl. spin hyperfine interaction (usually more)

Signal S



$$\frac{dS}{dB}$$



most important interaction!

(12)

$$\hat{S} \underline{\underline{A}} \hat{I}$$

\hookrightarrow coupling tensor

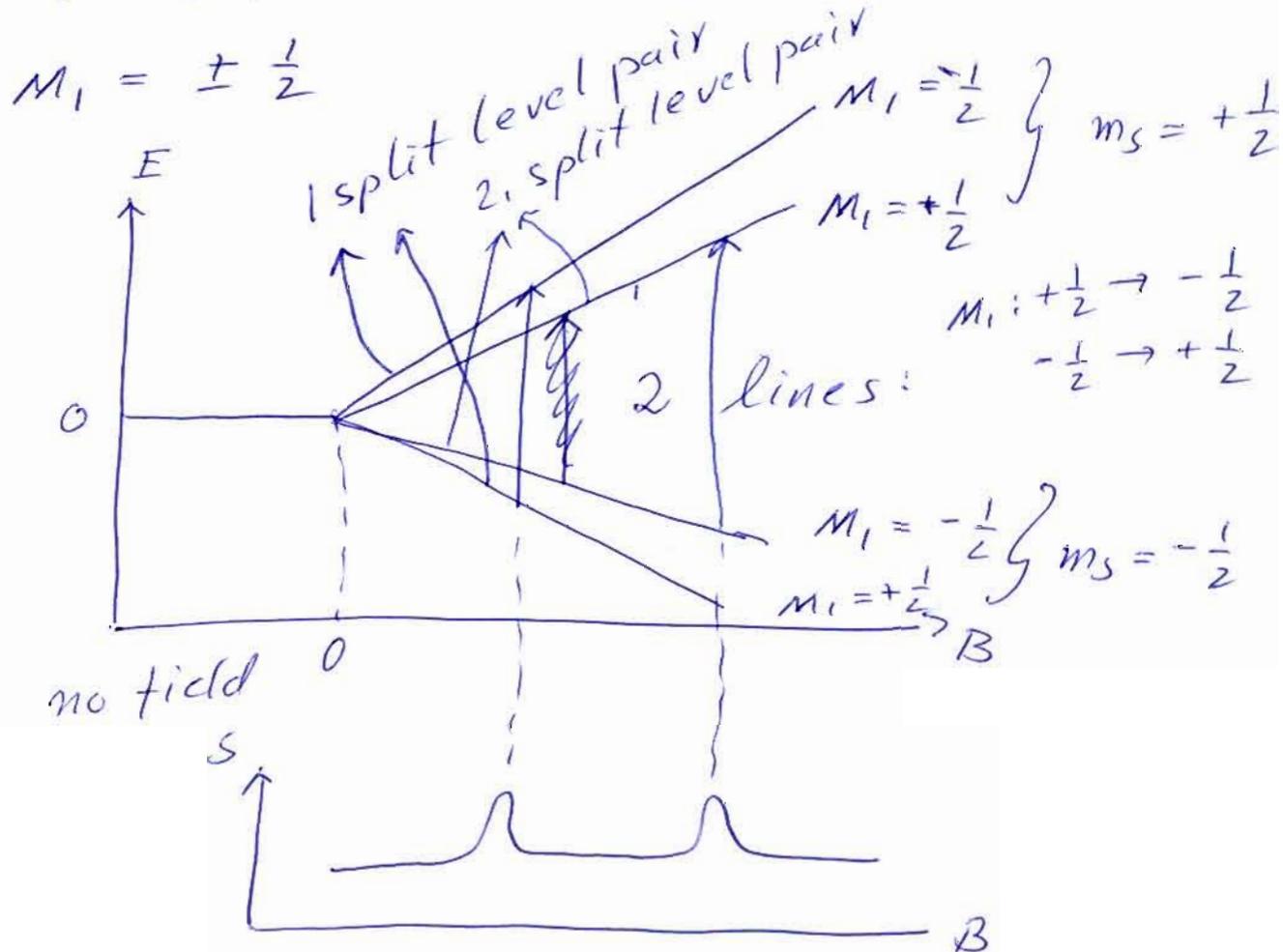
How many lines from ^{35}Cl ?

nuclear spin $I = \frac{3}{2}$

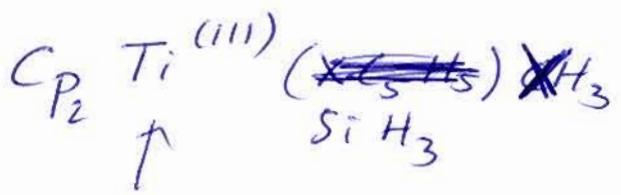
$\rightarrow (2I+1) M$ values: $\pm \frac{3}{2}, \pm \frac{1}{2}, 0$

lines from $-M$ to $+M \rightarrow 4$ lines

1 electron in H with $I = \frac{1}{2}$,



2 Signals



(13)

1 unpaired e! $X = {}^{14}_N {}^{31}P$

$X = {}^{31}P$ well separated coupling constants
both $I = \frac{1}{2}$

→ no overlap of the two spectra due to coupling of the Ti^{III} e-spin to

${}^{31}P$: $\alpha_p = 28.6$ G (Gauss)

and 1H : $\alpha_H = 4.3$ G

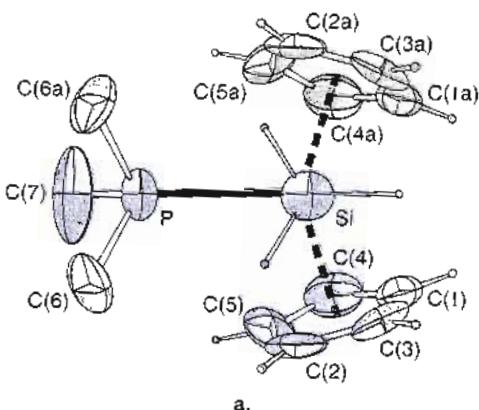
$X = {}^{14}N$: overlapping spectra:

$$\alpha_N = 1.75$$
 G

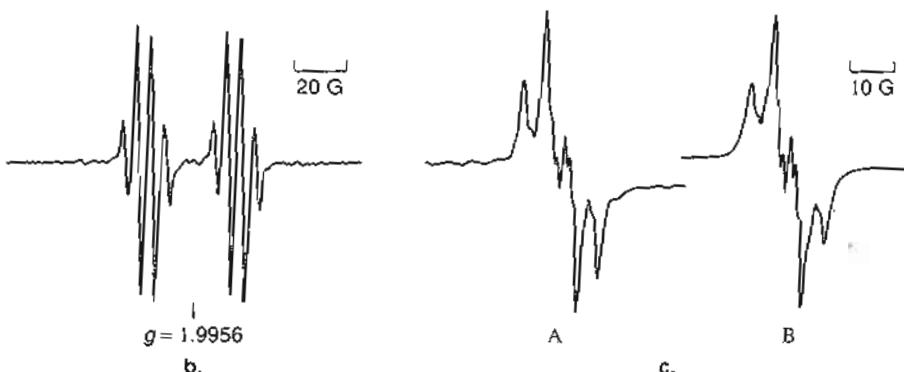
$$\alpha_H = 3.75$$
 G in this case

here: spectra must be simulated and compared to exp.

when they agree → coupling constants!

**FIGURE 14.44**

(a) A view of the structure of $\text{Cp}_2\text{Ti}(\text{SiH}_3)(\text{PMe}_3)$ looking along the Si-Ti bond with Ti hidden. (b) EPR spectrum of $\text{Cp}_2\text{Ti}(\text{SiH}_3)(\text{PMe}_3)$ in toluene at room temperature for well-separated hyperfine couplings. (c) EPR spectrum of $\text{Cp}_2\text{Ti}(\text{SiH}_3)(\text{PMe}_3)$ (A) with overlap of hyperfine couplings, along with a numerical simulation (B). Reproduced with permission from W. Hao, A. Lebuis, and J. F. Harrod, "Synthesis and structural characterization of $\text{Cp}_2\text{Ti}(\text{SiH}_3)(\text{PMe}_3)$," *Chem. Commun.* 1089 (1998), Figures a., b. and c., by permission of The Royal Society of Chemistry.



and the electron spin it is $a_H = 3.75 \text{ G}$. These are determined by simulating the spectrum. Such simulations are essential to the interpretation of many ESR spectra. Using computational methods, the values of overlapping hyperfine coupling constants can be deduced. Shown in Figure 14.44c, part B is a simulated spectrum which can be compared to the actual spectrum in Figure 14.44c, part A. The agreement in this case is not perfect, since small and complicated couplings to the protons of the pyridine ring are not included.

14.8 Mössbauer Spectroscopy

R. L. Mössbauer received the Nobel Prize in physics in 1961 for discovering the Mössbauer effect.

In 1958 the German physicist Rudolf Ludwig Mössbauer (b. 1929) discovered what has come to be known as the **Mössbauer effect**. It is concerned with the emission of γ (Greek *gamma*) rays, which under ordinary conditions are emitted with a considerable spread of wavelength. This is because of the recoil of the emitting nuclei. However, in Mössbauer's experiments the emitting nuclei were part of a crystal, the recoil of which is very small, and the γ rays are therefore emitted with an exceedingly narrow spread of wavelength. In some experiments the spread is as low as 1 part in 10^{13} . An important application of these highly homogeneous γ rays was to provide a crucial test of Einstein's theory of relativity. They have also found useful spectroscopic applications.

Obj Statistical mechanics

(39) -j

in 1 mol of a real system:

N_A molecules in the sample

but calculations with 10^{23} particles
not possible

statistics can calculate the most
probable behavior

only if there are a few particles
observed: fluctuations

(deviations from most probable
behavior)

before:

quantum mechanics (QM)

→ spectroscopy

now

QM → statistics

→ thermodynamic properties
needed: distribution of the
molecular energies

different forms of the
molecular energies:

(39)-2

degrees of freedom

the translation of a molecule can
happen in 3 directions, or linear
combinations of them

→ 3 translational degrees of
freedom along x , y , and z

each degree of freedom ~~and~~ yields
 $\frac{1}{2}k_B T$ average energy

$$\rightarrow \underset{\text{translational}}{\mathcal{E}_{\text{tr}}} = \mathcal{E}_x + \mathcal{E}_y + \mathcal{E}_z = \frac{3}{2}k_B T$$

average energy

equal distribution over the 3 in a
statistical sample

classical: Equipartition of energy

same part of energy goes on
average into each degree of freedom.

translations: all 3 equivalent (39) = 3

→ equipartition

non-linear molecules

3 degrees of rotational freedom
about the 3 axis

linear molecules

the rotation about the molecular axis is no degree of freedom

because in a diatomic molecule the moment of inertia is

$$I = \mu r_0^2$$

↗ ←

reduced mass distance from axis

if the rotation axis is along the molecule → distance of the atoms from rotation axis, $r_c = 0$

$$\rightarrow E_J = J(J+1) \frac{\hbar^2}{2I} \rightarrow \infty$$

→ no degree of freedom

further in molecules:

(39)-4

vibrational degrees of freedom

each normal mode is 1 degree of freedom

each atom has 3 coordinates x, y, z

→ for N_a atoms in molecule:

$3N_a$ degrees of freedom

non-linear molecules

3 translational and 3 rotational degrees of freedom

→ $3N_a - 6$ vibrations

linear molecules

3 translational and 2 rotational degrees of freedom

→ $3N_a - 5$ vibrations

monatomic gases:

He, Ne, Ar, Kr, Xe, Rn

only 3 translations

diatomic gases

(39) - 5

like H_2, O_2, F_2

$3N_a = 6$, 3 translations, 2 rotations

$6-5 = 1$ vibration (stretch)

linear triatomic gases

~~like~~ like CO_2

$3N = 9$, 3 translations, 2 rotations

$\rightarrow 9-5 = 4$ vibrations

non-linear triatomic gases

like H_2O vapor : $3N = 9$

3 translations, 3 rotations

$\rightarrow 9-6 = 3$ vibrations

molar heat capacities

C_{Vm} , C_V : constant volume

\rightarrow no work against pressure must be done

$\rightarrow C_{Vm}$ only from U_m

monatomic molecules

3 translational degrees of freedom:

$$U_m(\varepsilon) = \frac{3}{2} N_A k_B T = \frac{3}{2} R T$$

and

$$C_{Vm} = \frac{dU_m}{dT} = \frac{3}{2} R$$

$$\rightarrow \frac{C_{Vm}}{R} = \frac{3}{2} = 1.5$$

Same as experiment (table in
the book)

classical: each rotation gives on
average a contribution $\frac{1}{2}k_B T$ to U

→ diatomic (linear) molecules:

$$2 \text{ rotations} \rightarrow k_B T \text{ to } \frac{C_{Vm}}{R}$$

$$\rightarrow \frac{C_{Vm}}{R} = 1.5 + 1 = 2.5$$

nonlinear molecules:

3 rotations → $\frac{3}{2}k_B T$ contribution

$$\rightarrow \frac{C_{Vm}}{R} = 1.5 + 1.5 = 3.0$$

according to table not a (39)-7
very bad approximation

vibrations

Since there is kinetic and potential energy in each vibration

and both contribute $\frac{1}{2}k_B T$ on average

to $U \rightarrow k_B T$ for each vibration

or for $\frac{C_{v,m}}{R} : 1.0$ from each vibration

but the ~~classical~~ equipartition principle gives values that are far too large when compared to experimental ones

→ equipartition is not generally valid

for translations it is exact

for rotations it is approximation

for vibrations it is not valid at all

However, when T increases
the equipartition principle becomes
better valid the large T is
at low T , the equipartition breaks
down, especially for vibrations

Reason :

from quantum mechanics (QM) we
know: vibrational energy energy
levels are widely spaced
(at ~~room~~ room - T the energy spacing
between neighboring levels is so
large that almost only $v=0$ is
populated with vibrating molecules)

\Rightarrow energy cannot move freely
between the widely spaced
vibrational levels

\rightarrow equipartition not possible
at low T

transitions

only if enough energy is supplied

→ only at high T = high energy
(fast molecules)

the energy can distribute itself more and more freely between vibrational levels

the higher T becomes

Obj distribution of

(40)-1

energy among levels

question: how is energy distributed
among different degrees
of freedom?

an assembly or system:

collection of a large number N
of identical atoms or molecules

let us assume: the molecules are
independent of each other:

the state of 1 molecule is not
influenced by the presence of the
other ones

→ collection of states (QM) for
each molecule,

ordered such that

$$\epsilon_0 < \epsilon_1 < \epsilon_2 \dots \text{for each molecule}$$

the number of molecules (40)-2 populating each level: n_0, n_1, n_2, \dots

→ for any given, fixed total energy (a state of the system) there are many different ways to distribute the molecules among the levels

assume N molecules in the system and for example $n_0 = 3$ molecules in energy level ϵ_0

→ N possible choices to put the first molecule into ϵ_0

then $(N-1)$ choices are left to put the second one into ϵ_0

then $(N-2)$ choices are left to put the third one into ϵ_0

→ out of a system of N molecules, (40)-3

there are $N(N-1)(N-2)$ choices to put 3 molecules into Σ .

but the molecules are identical

→ it does not matter in which sequence we make the choices

each sequence is no new choice
(each sequence of choosing the 3)

take 3 molecules $a, b,$ and c

then the choices

abc 1. is a , 2. is b , 3. is c

bca 1. is b , 2. is c , 3. is a

are ~~iden~~ the same because we

cannot label identical molecules

→ all choices of the 3 in (40)-4

different sequence,

abc, bca, cba, acb, bac, cab

are the same.

so for 3 molecules, 6 identical

sequences: $6 = 3!$ three factorial

$$3! = 3 \cdot 2 \cdot 1 = 6$$

$$N! = N \cdot (N-1) \cdot (N-2) \cdot (N-3) \cdots 3 \cdot 2 \cdot 1$$

$$\rightarrow \frac{N(N-1)(N-2)}{3!}$$

possible and different ways to put 3 molecules out of N into ϵ .

now to put 2 molecules into ϵ ,

there are $\frac{(N-3)(N-4)}{2!}$ choices left

take the product for all levels together with the number of molecules in each level gives the

number of complexions

here the no. of ways to choose 3 molecules to put into ε_0 and 2 to put into ε_1 out of N identical molecules

= no. of complexions Ω is

$$\Omega = \frac{N(N-1)(N-2)(N-3)(N-4)}{3!2!}$$

→ total number of complexions to put n_i molecules out of N into the level ε_i , $i = 0, 1, 2, \dots$

$$\Omega = \frac{N!}{\prod_i n_i!}$$

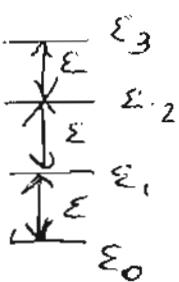
$$\prod_{i=1}^N x_i = x_1 \cdot x_2 \cdot x_3 \cdots \cdot x_N$$

Restriction :

total energy must stay the same when we distribute ~~the~~ the molecules over the levels

(40)-6

assume: 4 equally spaced levels
with spacing ε between them:



$$\varepsilon_0 = 0, \varepsilon_1 = \varepsilon, \varepsilon_2 = 2\varepsilon, \varepsilon_3 = 3\varepsilon$$

total energy assume to be 3ε
and that there are 3 molecules

$$\Rightarrow E_t = 3\varepsilon : 2 \text{ mol. in } \varepsilon_0 = 0, 1 \text{ mol. in } \varepsilon_3 = 3\varepsilon$$

$$\text{or } 3 \text{ mol. in } \varepsilon_1 = \varepsilon$$

$$\text{or } 1 \text{ mol. in } \varepsilon_0 = 0, 1 \text{ in } \varepsilon_1 = \varepsilon \text{ and } 1 \text{ in } \varepsilon_2 = 2\varepsilon$$

no other way possible when

$$E_t = 3\varepsilon$$

$$\Rightarrow 3 \text{ complexions, } 3 \text{ } 52^- \text{s}$$

Assume a state where all molecules are in different levels

$$\rightarrow n_i = 1 \quad \forall i \quad \forall = \text{for all}$$

$$\Omega = \frac{N!}{1!(1!) \cdots 1!} = N!$$

⇒ that state has the largest possible value of Ω

(40)-7

denominator = 1 smaller ~~not~~ not possible
nominator: $N!$ anyway for all Ω

⇒ the state with $n_i = 1 \forall i$
has the largest no. of complexions Ω

smallest possible change:

put not 1 but 2 mol. into the lowest level: $n_0 = 2$

and excite 1 into the now empty level → same energy

$$\text{now: } \Omega = \frac{N!}{2! 1! \dots} = \frac{1}{2} N!$$

no. of complexions for this smallest change state is much

smaller: $10^{23}!$ for the first state

$\frac{1}{2} 10^{23}!$ for this one

now assume 1 molecule to be in an excited state, and all other ($N-1$) molecules in the lowest state

$$\rightarrow \Omega = \frac{N!}{(N-1)! \cdot 1!} = N \ll N!$$

very large N , in the order of N_A :
 just 1 state, that one with the broadest possible distribution of all molecules on all levels will have a much larger Ω than all others

this state with largest Ω will give the most probable behavior of the system

Boltzmann distribution law

(40)-9

W : total no. of complexions

$$W = \sum_{\text{all states}} \Omega = \sum_{\text{all states}} \frac{N!}{\prod n_i!}$$

restrictions

$$\sum_i n_i = N$$

$$\text{energy} = \text{const.}$$

$$\sum_i n_i \epsilon_i = E$$

the largest Ω value is predominant over all other states

$$\Omega = \frac{N!}{\prod n_i!}$$

$$\ln \Omega = \ln N! - \sum_i \ln n_i$$

Stirling approximation:

if n large ($n > 10$):

$$\ln n! = n \ln n - n$$

$$\rightarrow \ln \Omega = \ln N! - \sum_i (n_i \ln n_i - n_i)$$

(40)-10

$$\delta \Omega = \sum_i \frac{\partial \Omega}{\partial n_i} \delta n_i = 0$$

change independent maximum
in Ω small changes condition
in cell n_i

$$\sum_i n_i = N$$

$\cancel{\text{if}}$ the δn_i are not cell independent,
but

$$\sum_i \delta n_i = 0 \text{ must hold}$$

$$\sum_i n_i \varepsilon_i = E = \text{const}$$

$$\rightarrow \sum_i \varepsilon_i \delta n_i = 0 \text{ must hold}$$

multiply by constants $\alpha, -\beta$:

$$\alpha \sum_i \delta n_i = 0$$

$$-\beta \sum_i \partial \varepsilon_i \delta n_i = 0$$

Lagrange multiplier method to
ensure that such conditions
hold:

$$\delta S = \sum_i \left(\frac{\partial S}{\partial n_i} + \alpha - \beta \varepsilon_i \right) \delta n_i = 0$$

must be true for all free
to chose variations δn_i

→ each brackett must be 0:

$$\frac{\partial S}{\partial n_i} + \alpha - \beta \varepsilon_i = 0$$

↑

difficult to work with

but when S is maximum,

$\ln S$ is also maximum

→ use of

$$\frac{\partial \ln S}{\partial n_i} + \alpha - \beta \varepsilon_i = 0$$

$$\frac{\partial \ln N!}{\partial n_i} = 0 \text{ since } N = \text{const.}$$

$$\text{and } \ln S = \ln N! - \sum_i (n_i \ln n_i - n_i)$$

(40)-12

$$\frac{\partial \ln S_2}{\partial n_i} = - \frac{\partial}{\partial n_i} (n_i \ln n_i - n_i)$$

$$= - \left(\ln n_i + \frac{n_i}{n_i} - 1 \right)$$

$$= - \ln n_i$$

into $\frac{\partial \ln S_2}{\partial n_i} + \alpha - \beta \varepsilon_i = 0$

$$\rightarrow \ln n_i = \alpha - \beta \varepsilon_i$$

$$n_i = e^\alpha e^{-\beta \varepsilon_i}$$

$$= A e^{-\beta \varepsilon_i} \quad A = e^\alpha$$

One can show: $\beta = \frac{1}{k_B T}$

$$\rightarrow n_i = A e^{-\frac{\varepsilon_i}{k_B T}}$$

no. of molecules: N

$$N = \sum_i n_i = A \sum_i e^{-\frac{\varepsilon_i}{k_B T}}$$

$$A = \frac{N}{\sum_i e^{-\varepsilon_i/k_B T}}$$

$$\rightarrow n_i = A e^{-\varepsilon_i/k_B T}$$

$$n_i = \frac{N e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}}$$

$$\boxed{\frac{n_i}{N} = \frac{e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}}}$$

Boltzmann distribution

fraction of molecules in
level ε_i at T

ratio for 2 levels i, j :

$$\frac{n_i}{n_j} = e^{-\frac{\varepsilon_i - \varepsilon_j}{k_B T}}$$

special case:

(40)-14

Maxwell distribution of
molecular speeds and
translational energies

derivation unimportant

but gives the proves that

$$\beta = \frac{1}{k_B T}$$

$$k_B = \frac{R}{N_A}$$

Probability of speeds along

x : dP_x , to find a molecule

with a speed within $v_x + dv_x$

derivation done in polar
coordinates

$\frac{dN}{N}$ fraction of molecules with
speeds within $v + dv$

probability to find molecules
with a speed within $u+du$ and u :

(46) -14a

$$dP = 4\pi B^3 e^{-mu^2 \beta/2} u^2 du$$

B: proportionality constant

$$\text{from } dP_x = B e^{-mu_x^2 \beta/2} du_x$$

Boltzmann for transl. energies $\frac{1}{2}mu_x^2$

(4π because $u+du$, u means two
spheres in u_x, u_y, u_z coordinates
with $4\pi u^2$ surface at u)

$$\frac{dN}{N} = \frac{4\pi B^3 e^{-mu^2 \beta/2} u^2 du}{4\pi \int_0^\infty B^3 e^{-mu^2 \beta/2} u^2 du} \leftarrow \frac{dN}{N}$$

$$\frac{dN}{N} = 4\pi \left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-mu^2 \beta/2} u^2 du$$

kinetic theory of ideal gases

$$\overline{u^2} = \frac{3RT}{N_A m} = \frac{3k_B T}{m} \quad \text{known}$$

and it must be

$$\bar{u^2} = \int_0^\infty u^2 \frac{dN}{N} = 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_0^\infty e^{-\frac{mu^2\beta}{2}} u^4 du \quad (40) - 146$$

$$\rightarrow \bar{u^2} = \frac{3}{m\beta}$$

$$\Rightarrow \frac{3}{m\beta} = \frac{3k_B T}{m}$$

$$\Rightarrow \beta = \frac{1}{k_B T}$$

$$\bar{u} = \sqrt{\int_0^\infty u \frac{dN}{N}} = \sqrt{\frac{8k_B T}{\pi m}}$$

most probable speed u_{mp}

at maximum of $\frac{dN}{N du}$

$$\cancel{u_{mp}} \cdot \frac{d}{du} \left\{ 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mu^2}{2k_B T}} u^2 \right\}_{u=u_{mp}} = 0$$

$$\rightarrow u_{mp} = \sqrt{\frac{2k_B T}{m}}$$

(40)-15

$$\rightarrow \frac{dN}{N} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mu^2}{2k_B T}} u^2 du$$

\rightarrow mean square speed:

$$\overline{u^2} = \frac{3k_B T}{m}$$

average speed: $\sqrt{\frac{8k_B T}{\pi m}}$

most probable speed $u_{mp} = \sqrt{\frac{2k_B T}{m}}$

Maxwell-Boltzmann distribution

of translational energies: $dE = d\left(\frac{1}{2}mu^2\right)$
 $= mu du$

$$\frac{dN}{N} = \frac{2\pi}{(\pi k_B T)^{3/2}} e^{-\frac{E/k_B T}{2}} E^{1/2} dE$$

average translational energy:

$$\bar{E} = \int_0^\infty E \frac{dN}{N} = \frac{3}{2} k_B T$$

$\frac{1}{2} k_B T$ for each direction!

Obj partition functions and (41)-1
thermodynamic functions from them

The partition function

Denominator of Boltzmann distribution: partition function or sum of states

Molecular partition function

$$q = \sum_i e^{-\varepsilon_i/k_B T}$$

levels: $\varepsilon_0 = 0 < \varepsilon_1 < \varepsilon_2 < \dots$

$$q = e^{-0/k_B T} + e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T} + \dots$$

= 1 + decreasing terms

if levels are very close together in energy (like for translation)

$\rightarrow q = 1 + \underline{\text{many}} \text{ terms close to 1}$

\rightarrow in normal volume (of N_A molecules),
300K, $q_{\text{transl.}} > 10^{30}$

other extreme:

(41)-2

widely spread levels

(like electronic levels):

$q = 1 + \text{very small terms}$

≈ 1

ψ_1 : first electronically excited

state: $18\ 310.5\ \text{cm}^{-1}$ above the
ground state:

$$18\ 310.5\ \text{cm}^{-1} \cong 3.64 \cdot 10^{-19}\ \mathcal{J}$$

$$\exp\left(-\frac{3.64 \cdot 10^{-19}\ \mathcal{J}}{k_B \cdot 300\ K}\right) = 7.4 \cdot 10^{-39}$$

rotational / vibrational levels

Spacings in between the extremes

rotational part:

$q > 1$ substantially

vibrational part:

$q \approx 1$ often

the partition function gives (41)-3
an indication of how many states
are accessible (how many can be
reached = occupied by molecules)

$T=0$: only ground state accessible
 $\rightarrow q=1$ at $0K$

T increasing: more and more states
become accessible $\rightarrow q$ increases
 $T \rightarrow \infty$ all states are accessible
= classical equipartition

degeneracy: g_i states of energy ϵ_i

$$\rightarrow q = \sum_i g_i e^{-\epsilon_i/k_B T}$$
$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/k_B T}}{q}$$

example : C-I bond

(41) - 4

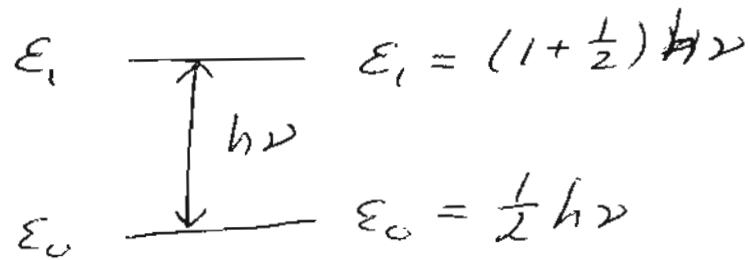
low frequency because of large iodine mass

→ higher vibrational levels are occupied

given: $\nu = 5.0 \cdot 10^{12} \text{ s}^{-1}$ at, $T = 298 \text{ K}$

calculate $\frac{n_8}{n_0}$, q , n_8/N

$$\varepsilon_i - \varepsilon_0 = i \cdot h\nu$$



$$\rightarrow \varepsilon_8 - \varepsilon_0 = 8h\nu = 2.65 \cdot 10^{-20} \text{ J}$$

$$\frac{n_i}{n_j} = e^{-\frac{(\varepsilon_i - \varepsilon_j)}{k_B T}} \rightarrow \frac{n_8}{n_0} = e^{-\frac{8h\nu}{k_B T}}$$

$$\frac{n_8}{n_0} = e^{-6.44} = 1.59 \cdot 10^{-3}$$

$$q = \sum_i e^{-\frac{\varepsilon_i}{k_B T}} \quad \text{all degeneracies}$$

$$g_i = 1$$

for vibrations

$$-\frac{\epsilon_i}{k_B T}$$

i	e
0	1
1	0.447
2	0.200
3	0.090
4	0.040
8	0.002

$$\rightarrow q \approx 1.8$$

easier way later

$$\frac{n_8}{N} = \frac{e^{-(\epsilon_8 - \epsilon_0)/k_B T}}{q} = \frac{e^{-6.44}}{1.8} = 8.9 \cdot 10^{-4}$$

canonical partition function

$q \rightarrow$ single molecule

N molecules

\rightarrow canonical partition function Q
for the system

if $N = N_A : 1 \text{ mol} \rightarrow$ molar partition
function

$$Q = \sum_i e^{-\epsilon_i/k_B T} \quad (41)-6$$

now summation over all levels of
all molecules

1) ideal crystal (ordered,
no imperfections)

all molecules are localized

and are distinguishable, countable

each molecule ~~is~~ has a label:

its position in the lattice

$$Q = \sum_{ijk\cdots} \exp \left[-\frac{\epsilon_i^a + \epsilon_j^b + \epsilon_k^c \cdots}{k_B T} \right]$$

molecules a, b, c, ...

$$= \left[\sum_i \exp \left(-\frac{\epsilon_i^a}{k_B T} \right) \right] \left[\sum_j \exp \left(-\frac{\epsilon_j^b}{k_B T} \right) \right] \cdots$$

countable molecules, all the
same kind of molecules:

$$Q = \left(\sum_i e^{-\epsilon_i/k_B T} \right)^N = q^N$$

2) gas

no fixed position of molecules
 molecules have no label (like lattice position) and cannot be distinguished or counted in a given sequence

state with a given energy E is the same, when we interchange the molecules in their levels

$$\varepsilon^a, \varepsilon^b, \dots$$

$\Rightarrow N!$ permutations which do not change the state

\rightarrow molecules indistinguishable:

$$Q = \frac{q^N}{N!} \quad \text{Stirling: } n! = \frac{n^n}{e^n}$$

when $n > 10$

$$\rightarrow Q = \left(\frac{qe}{N} \right)^N$$

Thermodynamic functions

(41)-8

from partition functions

possible for all of them
internal energy U :

all molecules in lowest energy

→ U_0 lowest internal energy

from $\Omega \approx U - U_0$ can be obtained

assume an ^{assembly}~~ensemble~~ (α group)
of N^* assemblies (sub-assemblies)
= parts of the system = assembly)

each one of them with energies

E_1^*, E_2^*, \dots

of which each one is present

n_1^*, n_2^*, \dots times in the assembly

→ average value gives $U - U_0$: (41) - 8

$$U - U_0 = \frac{1}{N^*} \sum_i n_i^* E_i$$

$$N^* = \sum_i n_i^*$$

Boltzmann: $\frac{n_i^*}{N^*} = \frac{g_i \exp(-E_i^*/k_B T)}{Q}$

$$Q = \sum_i g_i \exp(-E_i^*/k_B T)$$

ave

~~$U - U_0$~~ average energy:

$$\begin{aligned} U - U_0 &= \sum_i \frac{n_i^*}{N^*} E_i^* \\ &= \frac{\sum_i g_i E_i^* e^{-(E_i^*/k_B T)}}{Q} \end{aligned}$$

practice: just ignore U_0

(falls out in all measurable)

$$\Delta U \quad \frac{\partial}{\partial T} e^{-E_i^*/k_B T} = -\left(\frac{1}{k_B T^2}\right) E_i^* e^{-E_i^*/k_B T}$$

look at Q :

$$\frac{\partial Q}{\partial T} \Big|_V = \frac{1}{k_B T^2} \sum_i g_i E_i^* e^{-E_i^*/k_B T}$$

$\hookrightarrow -(-\cdots) \rightarrow +$

$$U = U_0 = \frac{\sum_i g_i E_i^* \exp(-E_i^*/k_B T)}{Q} \quad (41) - 10$$

$$= \frac{k_B T^2}{Q} \left. \frac{\partial Q}{\partial T} \right|_V$$

$$= k_B T^2 \left. \frac{\partial \ln Q}{\partial T} \right|_V$$

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V$$

entropy : $\int_{S_0}^S dS = \int_0^T \frac{C_V}{T} dT$

\downarrow \downarrow
 $S - S_0$ again S_0

from $C_V = \left. \frac{\partial U}{\partial T} \right|_V$

and partial integration

$$\Rightarrow S = k_B T \left. \frac{\partial \ln Q}{\partial T} \right|_V + k_B \ln Q$$

$$= \frac{U - U_0}{T} + k_B \ln Q$$

$S_0 = k_B \ln Q_0$ cancels out

→ Helmholtz energy: (41)-11

$$A = U - TS = \tilde{U} - \tilde{U} + U_0 - k_B T \ln Q$$

$$\Rightarrow A - U_0 = -k_B T \ln Q$$

$$T = 0 \Rightarrow TS = 0$$

pressure: $P = -\frac{\partial A}{\partial V}\Big|_T = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T$

→ enthalpy $H = U + PV$

$$= U + Nk_B T$$

$$H - U_0 = k_B T^2 \frac{\partial \ln Q}{\partial T}\Big|_V + Nk_B T$$

Gibbs energy:

$$G = A + PV \pm A + Nk_B T$$

$$\rightarrow G - U_0 = -k_B T \ln Q + Nk_B T$$

Two compounds a, b:

(41)-12

$$Q = \frac{q_a^{N_a} q_b^{N_b}}{N_a! N_b!}$$

chem. potential: $\mu_a = \frac{\partial A}{\partial N_a} \Big|_{T,V}$

$$= -k_B T \frac{\partial \ln Q}{\partial N_a} \Big|_{T,V}$$

$\ln Q \rightarrow$ stirling formula

$$\begin{aligned} \rightarrow \frac{\partial \ln Q}{\partial N_a} \Big|_{T,V} &= \ln q_a - \ln N_a \\ &= \ln \frac{q_a}{N_a} \end{aligned}$$

molecular chemical potential:

$$\mu_a = -k_B T \ln \frac{q_a}{N_a}$$

$$Q = \frac{q_a^{N_a} q_b^{N_b}}{N_a! N_b!}$$

(41)-13

$$\rightarrow \ln Q = N_a \ln q_a + N_b \ln q_b$$

$$- \ln N_a! - \ln N_b!$$

$$\text{Stirling: } \ln n! = n \ln n - n$$

$$\rightarrow \ln Q = N_a \ln q_a - N_a \ln N_a + N_a$$

$$+ N_b \ln q_b - \ln N_b!$$

\rightarrow directly

$$\frac{\partial \ln Q}{\partial N_a}$$

Obj : complete partition function (42)-1

$$E_t = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e + \varepsilon_n \quad \text{additive}$$

$$\rightarrow q = q_t \cdot q_r \cdot q_v \cdot q_e \cdot q_n \quad \text{multiplicative}$$

translation rotation vibration electronic nuclear

example:

$$q = \sum_i e^{-\frac{\varepsilon_i}{k_B T}} = \sum_{j,k} e^{-\frac{(\varepsilon_j^r + \varepsilon_k^v)}{k_B T}}$$

$$= \sum_j e^{-\frac{\varepsilon_j^r}{k_B T}} \cdot \sum_k e^{-\frac{\varepsilon_k^v}{k_B T}} = q_r \cdot q_v$$

Translation

ideal monatomic gases: He, Ne, Ar, ...

at normal T only translation

($\varepsilon_e, \varepsilon_n$ spacings too large)

$$\varepsilon_t = \varepsilon_x + \varepsilon_y + \varepsilon_z$$

$$\rightarrow q_t = q_x \cdot q_y \cdot q_z$$

3-dim. box:

$$\epsilon_t = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

extremely small spacing

→ instead of \sum over n

→ Integration:

~~$$q_x = \sum_{n_x=0}^{\infty} \exp \left[-\frac{h^2}{8ma^2 k_B T} n_x^2 \right]$$~~

$$= \int_0^{\infty} \exp \left[-\frac{h^2}{8ma^2 k_B T} n_x^2 \right] d n_x$$

$$= \frac{a}{h} \sqrt{2\pi m k_B T}$$

$$q_t = q_x q_y q_z = \frac{V}{h^3} \left(\sqrt{2\pi m k_B T} \right)^3$$

$$= \text{const.} \cdot T^{3/2} \cdot V \quad , \quad V = abc$$

1 H atom at 300K in 1m^{-3}

(42)-3

$$m_H = \frac{1.008 \text{ kg/mol}}{6.022 \cdot 10^{23} \text{ mol}^{-1}}$$

$$= 1.674 \cdot 10^{-27} \text{ kg}$$

$$\rightarrow q_t = 9.89 \cdot 10^{29}$$

Large because of small
level spacing

rot./vib. q -s much smaller

N indistinguishable particles

$$Q = \left(\frac{qe}{N}\right)^N$$

$$\ln Q = N \ln \left[\frac{V}{N h^3} (2\pi m k_B T)^{3/2} \right] + N$$

$$(\ln e^N = N \ln e = N)$$

$$= N \ln \left[\text{const. } VT^{3/2} \right] + N$$

(42) - 4

$$U_m: U_0 = 0 \quad (U_m \text{ molar})$$

for translation the lowest level
is shifted to 0

$$\rightarrow U_m \text{ actually is } U_m - U_{0,m}$$

molar enthalpy:

$$\ln Q_m = N_A \ln [\text{const.} \cdot VT^{3/2}] + N_A$$

$$\text{molar: } N = N_A$$

$$U_m = k_B T^2 \left. \frac{\partial \ln Q_m}{\partial T} \right|_V$$

$$\frac{\partial \ln x}{\partial y} = \frac{1}{x} \frac{\partial x}{\partial y}$$

$$U_m = k_B T^2 \underbrace{\text{const}^{-1} V_m^{-1} T^{-3/2}}_{1/x} \underbrace{\text{const.} V_m^{3/2} \cdot T^{1/2}}_{\partial x / \partial T}$$

$$= \frac{3}{2} N_A k_B T$$

$$P_m V_m = k_B T + \frac{\partial \ln Q_m}{\partial V} \cdot V_m$$

(42) - 5

$$= k_B T N_A \underbrace{\text{const}^{-1} V_m^{-1}}_{1/x} T^{-3/2} \underbrace{\text{const.} T^{3/2}}_{\frac{\partial x}{\partial V}} \cdot V_m$$

$$= N_A k_B T$$

$$H_m = U_m + P_m V_m = \left(\frac{3}{2} + 1\right) N_A k_B T$$

$$= \frac{5}{2} N_A k_B T$$

heat θ_m for T-increase by ΔT :

at $P = \text{const.}$

$$\theta_m = \Delta H_m = \frac{5}{2} N_A k_B \Delta T$$

Sackur - ~~Teddr~~ Tetrode equation:

$$S_m = \frac{U_m - U_{0,m}}{T} + k_B \ln Q$$

$$= \frac{3}{2} R + R \ln \left[\frac{V_m}{N_A h^3} (2\pi m k_B T)^{3/2} \right]$$

$$PV_m = N_A k_B T \rightsquigarrow P$$

rotations

$$\mathcal{E}_r = \frac{J(J+1)}{8\pi^2 I} \frac{\hbar^2}{2}$$

linear rigid rotor

$$q_r = \sum_i g_i e^{-\frac{\epsilon_i / k_B T}{2}}$$

$$= \sum_J (2J+1) \exp \left[- \frac{J(J+1) \hbar^2}{8\pi^2 I k_B T} \right]$$

if level spacing $\Delta E < k_B T$

→ integration (J from 0 to ∞):

$$\rightarrow q_r = \frac{8\pi^2 I k_B T}{\hbar^2}$$

for asymmetric molecules correct

(all levels accessible)

symmetric molecules (H_2, CO_2, C_2H_2):

some levels are ~~forbidden~~

depending on geometry

symmetry number σ

asymmetric: $\bar{\sigma} = 1$

(42) $\Rightarrow 7$

linear, symmetric: $\bar{\sigma} = 2$

$$q_r = \frac{8\pi^2 I k_B T}{5h^2}$$

general for linear molecules

Q_r : for indistinguishable molecules

$$Q = \left(\frac{q_t q_r \dots e}{N} \right)^N$$

$$\left(\frac{e}{N} \right)^N \text{ included in } Q_t = \left(\frac{q_t e}{N} \right)^N$$

$$\Rightarrow Q_r = q_r^N$$

$$U_{m,r} = N_A k_B T^2 \frac{\partial \ln q_r}{\partial T} = RT$$

$\bar{\sigma}$ cancels out

general molecules:

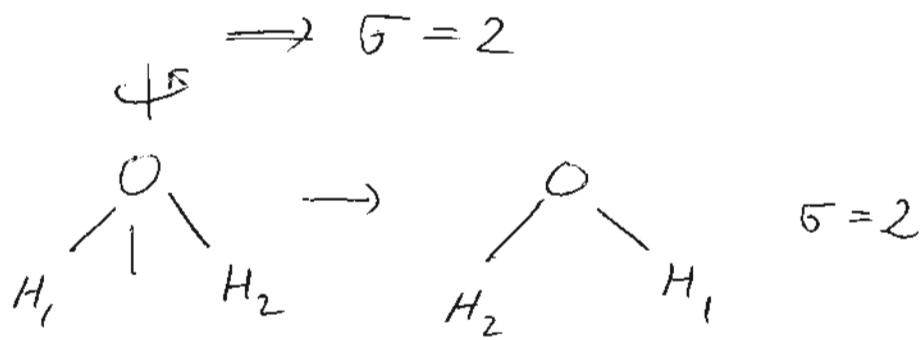
$$q_r = \frac{8\pi^2}{5h^3} \left(8\pi^3 I_A I_B I_C \right)^{1/2} (k_B T)^{3/2}$$

moments of inertia
about the 3
principal axes

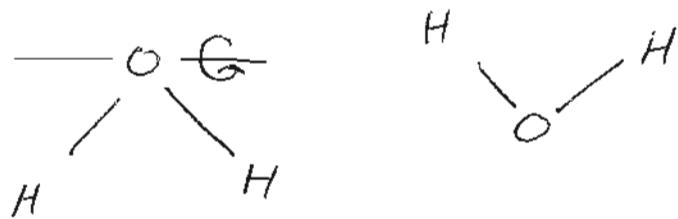
rotation about principal axis (42)-8
in CO_2 :

$$\begin{matrix} \text{O}_1 & = & \text{C} & = & \text{O}_2 \\ & & | & & \\ & & \phi & & \end{matrix} \rightarrow \begin{matrix} \text{O}_2 & = & \text{C} & = & \text{O}_1 \end{matrix}$$

2 different forms of the same geometry (indistinguishable)



other rotations change geometry in space \rightarrow cannot lead to same structure: $\text{G}=1$ for those:



(42)-9

$$H_2 : r_0 = 0.074 \text{ pm}$$

q_r at 300 K, $\ln Q_r$ for N_A molecules?

$$I = \mu r_0^2 = m_H r_0^2 = 4.583 \cdot 10^{-48} \text{ kg m}^2$$

$$\Gamma = 2 \rightarrow q_r = \frac{8\pi^2 I k_B T}{5 h^2} = 1.707$$

unusually small, because m_H - very small and also r_0 small

typically: q_r -s between 10 - 1000 smaller than q_t : wider level spacing

$$\ln Q_r^m = N_A \ln q_r = 3.22 \cdot 10^{23}$$

vibration

level spacing $> k_B T$ at 300 K

→ only few terms in q_v
important

$$\epsilon_v = (v + \frac{1}{2}) \hbar \nu$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

classical oscillator frequency

energies relative to $\nu=0$ level
(zero-point level set to 0)

$$\rightarrow E_v = v \hbar \nu$$

(relative to zero-point level)

$$\overline{q}_v = \sum_{v=0}^{\infty} e^{-\frac{v \hbar \nu}{k_B T}}$$

for relative to zero-point

integral not possible here

because of level spacing

$$x \equiv e^{-\frac{\hbar \nu}{k_B T}}$$

$$\rightarrow e^{-\frac{v \hbar \nu}{k_B T}} = x^v$$

$$\rightarrow \overline{q}_v = 1 + x + x^2 + \dots \text{ geometric series}$$

(42)-11

$$S = \sum_{v=0}^{\infty} x^v$$

$$= 1 + x + x^2 + \dots$$

$$\underline{S} = 1 + x(1 + x + \dots)$$

$$= 1 + x \cdot S$$

$$\rightarrow (1-x) \cdot S = 1, \quad S = \frac{1}{1-x}$$

possible if S is absolutely convergent

$$\rightarrow \bar{q}_v = \frac{1}{1-x}$$

$$\bar{q}_v = \frac{1}{1 - e^{-\hbar\nu/k_B T}}$$

$$= \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} = \frac{e^{\theta_{\text{vib}}/T}}{e^{\theta_{\text{vib}}/T} - 1}$$

characteristic temperature:

$$\theta_{\text{vib}} = \frac{\hbar\nu}{k_B}$$

$$\theta_{\text{vib}} \gg T : \bar{q}_v \approx 1$$

$$\theta_{\text{vib}} \ll T : e^{-\theta_{\text{vib}}/T} \approx 1 - \frac{\theta_{\text{vib}}}{T}$$

if $\theta_{vib} \ll T$:

(42)-12

$$\bar{q}_v \approx \frac{T}{\theta_{vib}}$$

$$H_2: \theta_{vib} = 6210 K$$

$$T = 300 K : q_v \approx \frac{1}{1 - 10^{-9}} = 1$$

$$T = 3000 K : q_v = 1.144$$

back to real energy zero:

$$\epsilon_v = \frac{1}{2} h\nu + v h\nu$$

$$\rightarrow \exp\left[-\frac{\epsilon_v}{k_B T}\right] = \exp\left[-\frac{h\nu}{2k_B T}\right] \exp\left[-\frac{vh\nu}{k_B T}\right]$$

$$\rightarrow q_v = e^{-\frac{\theta_{vib}/2}{T}} \cdot \bar{q}_v$$

N oscillators:

$$Q_v = q_v^N \quad (\text{other factors in } Q_t)$$

$$\ln Q_v = N \ln e^{-\frac{\theta_{vib}/2}{T}} \bar{q}_v = -N \underbrace{\left(\frac{\theta_{vib}}{2T} + \right)}_{+ \ln(1 - e^{-\theta_{vib}/T})}$$

$$\int_{S_0}^S dS = \int_0^T \frac{C_V}{T} dT$$

$$S - S_0 = \int_0^T \frac{C_V}{T} dT \quad ①$$

$$U = U_0 + k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \underbrace{\left(\frac{\partial U_0}{\partial T} \right)_V}_{''0''} + k_B \frac{\partial}{\partial T} \left[T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \right]$$

$$= k_B \left[T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_V + 2T \left(\frac{\partial \ln Q}{\partial T} \right)_V \right]$$

$$S - S_0 = k_B \int_0^T \left[T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_V + 2T \left(\frac{\partial \ln Q}{\partial T} \right)_V \right] dT$$

$$= \int_0^T \frac{C_V}{T} dT$$

$$k_B 2 \int_0^T \frac{\partial \ln Q}{\partial T} dT = 2k_B \ln Q - 2k_B \ln Q_0$$

$$k_B \int_0^T T \frac{\partial^2 \ln Q}{\partial T^2} dT$$

$$(uv)' = u'v + uv'$$

$$\rightarrow uv' = (uv)' - u'v$$

$$u = T$$

$$v' = \frac{\partial^2 \ln Q}{\partial T^2}$$

$$\int_{x_0}^x uv' dx = \int_{x_0}^x (uv)' dx - \int_{x_0}^x u'v dx$$

$$= uv - (uv)_0 - \int_{x_0}^x u'v dx$$

$$k_B \int_0^T T \frac{\partial^2 \ln Q}{\partial T^2} dT$$

\downarrow
 u \downarrow
 v'

(2)

$$= k_B T \frac{\partial \ln Q}{\partial T} \Big|_0^T - k_B \int_0^T \frac{\partial \ln Q}{\partial T} dT$$

\downarrow
 u \downarrow
 v \downarrow
 $u' = 1$ v

$$\int \frac{\partial^2 \ln Q}{\partial T^2} dT = \frac{\partial \ln Q}{\partial T} + C$$

\downarrow
 v' v

$$k_B \int_0^T T \frac{\partial^2 \ln Q}{\partial T^2} dT$$

$$= k_B T \frac{\partial \ln Q}{\partial T} - k_B \ln Q \Big|_0^T$$

0 for $T=0$

$$= k_B T \frac{\partial \ln Q}{\partial T} - k_B \ln Q + k_B \ln Q_0$$

$$S - S_0 = k_B T \frac{\partial \ln Q}{\partial T} - k_B \ln Q + k_B \ln Q_0$$

$$+ 2k_B \ln Q - 2k_B \ln Q_0$$

$$S - S_0 = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q - k_B \ln Q_0$$

since $S_0 = k_B \ln Q_0$, it cancels ③

$$\Rightarrow S = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q$$

$$U - U_0 = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

$$k_B T \frac{\partial \ln Q}{\partial T} = \frac{U - U_0}{T}$$

$$\Rightarrow S = \frac{U - U_0}{T} + k_B \ln Q$$

Obj: thermodynamic functions from statistics

$$U_v = k_B T^2 \left(\frac{\partial \ln Q_v}{\partial T} \right)_v$$

$$\begin{aligned}
 &= -Nk_B T^2 \left[-\frac{\theta_{vib}}{2T^2} + \frac{1}{1-e^{-\theta_{vib}/T}} \left[e^{-\frac{\theta_{vib}}{T}} \left(1 + \frac{\theta_{vib}}{T^2} \right) \right] \right] \\
 &\quad \cancel{\text{cancels}} \quad \cancel{\text{T}^2 \text{ cancels}} \quad \frac{\partial \ln x}{\partial x} = \frac{1}{x} \quad \frac{\partial(1-e^{-x})}{\partial x} = e^{-x} \quad \frac{\partial x}{\partial T} \\
 &\quad \left(\frac{1}{T^2} \text{ in } [-] \right) \quad = \frac{\partial}{\partial T} \left(-\frac{\theta_{vib}}{T} \right) \\
 &\quad \frac{e^{-x}}{1-e^{-x}} \cdot \cancel{\frac{e^x}{e^x}} = \frac{1}{e^x - 1}
 \end{aligned}$$

$$U_v = Nk_B \left[\frac{\theta_{vib}}{2} + \frac{\theta_{vib}}{e^{\theta_{vib}/T} - 1} \right]$$

$$U_{om,v} = N_A \frac{\hbar\nu}{2} = \frac{1}{2} N_A k_B \theta_{vib} \quad (\theta_{vib} = \frac{\hbar\nu}{k_B})$$

$$= \frac{1}{2} R \theta_{vib}$$

$$\rightarrow (U_v - U_{ov})_m = \frac{R \theta_{vib}}{e^{\theta_{vib}/T} - 1}$$

also possible from \overline{q}_v direct

$$h\nu \ll k_B T \Rightarrow \frac{\Theta_{vib}}{T} \rightarrow 0$$

(43)-2

$$\rightarrow e^{\Theta_{vib}/T} \approx 1 + \frac{\Theta_{vib}}{T}$$

$$\rightarrow (U_v - U_{vo})_m \approx RT$$

classical result for high T !

$$298\text{ K} : RT = 2480 \text{ J/mol classical}$$

$$\text{if } h\nu = 2 \cdot 10^{-20} \text{ J} \rightarrow \frac{\Theta_{vib}}{T} = \frac{h\nu}{k_B T} = 4,9$$

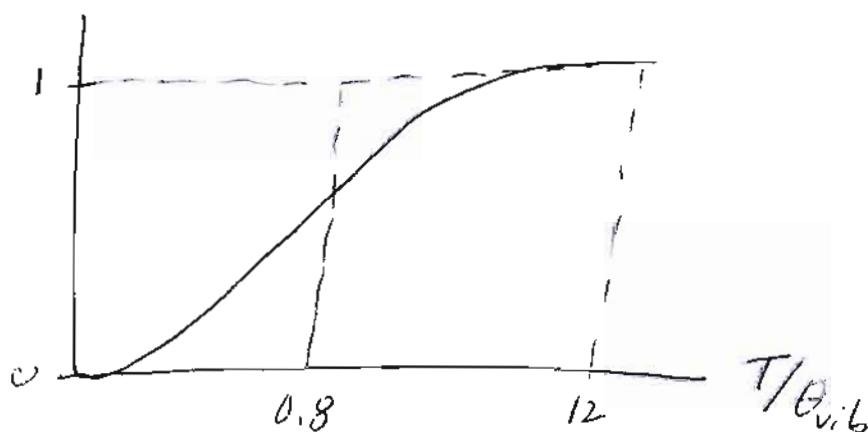
\rightarrow correct QM - result:

$$(U - U_o)_{v,m} = 91 \text{ J/mol}$$

$$C_v(vib) = \left. \frac{\partial U_v}{\partial T} \right|_V$$

$$\rightarrow \frac{C_v(vib)}{R} = \left(\frac{\Theta_{vib}}{T} \right)^2 \frac{e^{\Theta_{vib}/T}}{(e^{\Theta_{vib}/T} - 1)^2}$$

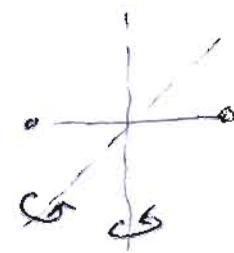
C_v/R Einstein function



diatomics: vib + rot/trans.

(43)-3

$$\frac{C_V}{R} = \frac{5}{2} + \bar{C}_V(\text{vib})$$



2 rotation axes

$\rightarrow \frac{5}{2}$ from rot.

1 Einstein function for each ν_i ,
added as factor if

different vibration $\nu_1, \nu_2 \dots$

(normal modes)

$$q = q_t q_r q_v^{s_1} q_v^{s_2} \dots$$

electronic partition function

usually: even wider level spacing
than in vib.

in H_2 for the first excited state:

$$\Delta E = 10.2 \text{ eV}$$

$\rightarrow q_e$ close to 1

if $\frac{\Delta E}{k_B} > 5K$ contribution can be
neglected

(43)-4

degeneracy:

electronic angular momentum of atoms:
quantum number j $\rightarrow 2j+1$ possible levels with equal energy

H: excited states can be ignored!

$$q_e(H) = 1$$

$$\begin{matrix} {}^3P_J \\ JK \\ S=1 \quad L=1 \end{matrix}$$

$$O: \quad {}^3P_0 \quad 226.1 \text{ cm}^{-1} \quad 1 \text{ state}$$

$$J =$$

$${}^3P_1 \quad 157.4 \text{ cm}^{-1} \quad 3 \text{ states}$$

$$L+S = 2$$

$${}^3P_2 \quad \text{lowest: } 0 \quad 5 \text{ states}$$

$$L+S-1 = 1$$

$$L-S = 0$$

$$q_e = 5e^{-\frac{E}{k_B T}} + 3e^{-\frac{157.4 \text{ cm}^{-1} hc}{k_B T}}$$

$$+ 8e^{-\frac{226.1 \text{ cm}^{-1} hc}{k_B T}}$$

$$= 8.97$$

most molecules have a ${}^1\Sigma$
ground state+ excited states high enough to be
neglectedexceptions: O_2, N_2^0 , free radicals

nuclear partition function

(43)-45

for exact calculations of absolute values of e.g. U, H, \dots

nuclear spins important

but no effects on energy changes,
e.g. on Gibbs energy changes

→ no effects on equilibrium constants

internal or thermal energy function:

$$U_{th} = U - U_0$$

Value at $T=0$

= all molecules in ground state
enthalpy function $H_f = \frac{H - H_0}{T}$

Gibbs energy function $G_f = \frac{G - H_0}{T}$

no large variations with T

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \rightarrow U_{th} = U - U_0 = \int C_V dT$$

→ U_{th} can be obtained from
 C_V measurements

or from partition function

$$H = U + PV$$

(43) - 5

$$H - \underline{U}_0 = U - U_0 + PV$$

$$1 \text{ mol: } H_m - \underline{U}_{0m} = U_m - U_{0m} + RT$$

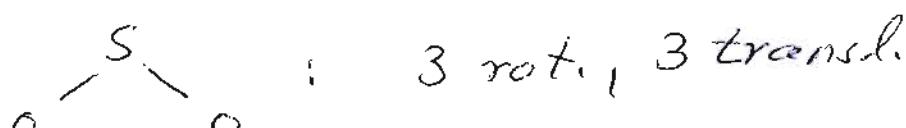
↑
ideal gas

$$U - U_0, H - U_0 \text{ for 1 mol } SO_2 \text{ at } 298K$$

trans/rot levels: classical treatment

unimportant

$$\bar{\nu} \text{ given}, q_e = 1$$



$$\rightarrow 6 \cdot \frac{1}{2}RT \text{ to DL}$$

$$= 6 \cdot 1243.4 \text{ J/mol} = 2 \cdot 3730.3 \text{ J/mol}$$

$$\mathcal{E}_1 = hc\bar{\nu}_1 (1151.4 \text{ cm}^{-1}) = 2.28 \cdot 10^{-20} \text{ J}$$

$$\mathcal{E}_2 = hc\bar{\nu}_2 (517.7 \text{ cm}^{-1}) = 1.03 \cdot 10^{-20} \text{ J}$$

$$\mathcal{E}_3 = hc\bar{\nu}_3 (1361.8 \text{ cm}^{-1}) = 2.70 \cdot 10^{-20} \text{ J}$$

(43) - F

$$\frac{\theta_{vib}}{T} = \frac{hc\bar{\nu}}{k_B \cdot 298K}$$

$$U - U_0 = \sum \frac{R\theta_{vib}}{e^{\theta_{vib}/T} - 1}$$

$$\bar{\nu} \quad \frac{\theta_{vib}}{T} \quad (U - U_0)_{vib}$$

$$\Sigma_1 \quad 5.54 \quad 54.3 \text{ J/mol}$$

$$\Sigma_2 \quad 2.50 \quad 555.9 \text{ J/mol}$$

$$\Sigma_3 \quad 6.57 \quad 22.9 \text{ J/mol}$$

$$\rightarrow U - U_0 = 2 \cdot 3730.2 \text{ J/mol}$$

$$+ (54.3 + 555.9 + 22.9) \text{ J/mol}$$

$$= 8093.5 \text{ J/mol}$$

$$H - H_0 = U - U_0 + RT = 10571.2 \text{ J/mol}$$

↓
2477 J/mol

in reactions: $\Delta H = \sum (H - H_0)_{\text{Product}}$

$- \sum (H - H_0)_{\text{Reactants}}$

Gibbs: $G = H - TS$

$$\frac{G - H_0}{T} = \frac{H - H_0}{T} - S$$

Equilibrium Constants

for reactions from thermodynamics:

$$\Delta H_T^\circ \xleftarrow{\text{therm.}} = \Delta H_0^\circ + \Delta (H_T^\circ - H_0^\circ)$$

$$\downarrow \qquad \qquad \qquad \downarrow$$

$$\sum_{\text{Prod.}} - \sum_{\text{React.}}$$

absolute zero

Gibbs energy:

$$\frac{\Delta G_T^\circ}{T} = \frac{\Delta H_0^\circ}{T} + \frac{\Delta (G_T^\circ - H_0^\circ)}{T}$$

$$H_T^\circ - H_0^\circ, G_T^\circ - H_0^\circ$$

from partition function

e.g. from experiment ΔH_T° is known

$$\rightarrow \Delta H_0^\circ \rightarrow \Delta G_T^\circ$$

$$\text{Then: } \Delta G_T^\circ = -RT \ln K$$

standard state: 1 bar pressure

$\Rightarrow K_p$ in units containing bar

example:

(44)-2

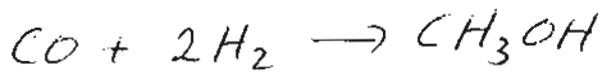


Table 15.6 (I think)

→ ~~not~~ ΔG_f° and K_p at 1000 K

and standard enthalpy change at
298 K

$$\Delta H_{298K}^\circ = \Delta H_{f,298}^\circ (CH_3OH) - \Delta H_{f,298}^\circ (CO) \xleftarrow{\text{measured}} \text{Appendix}$$
$$(-200.66 + 0^{110.53} - 0) \text{ kJ/mol}$$
$$- 2\Delta H_{f,298}^\circ (H_2)$$
$$= -90.13 \text{ kJ/mol}$$

standard enthalpy function (15.6) calculated

$$\Delta(H_{298}^\circ - H_0^\circ) = (H_{298}^\circ - H_0^\circ) \quad \text{as discussed before}$$



$$= -14.18 \text{ kJ/mol}$$

$$\Delta H_0^\circ = \Delta H_{298}^\circ - \Delta(H_{298}^\circ - H_0^\circ)$$

$$\xleftarrow{T=0} = 75.95 \text{ kJ/mol}$$

$$\Delta G_{1000}^\circ = \Delta H_0^\circ + T \Delta \left(\frac{G^\circ - H_0^\circ}{T} \right) \xleftarrow{1000K}$$

$CH_3OH - CO - 2H_2$

$$(-257.65 \text{ } CH_3OH + 204.18 \text{ } CO + 2 \cdot 137.07 \text{ } H_2)$$

$$= 144.4 \text{ kJ/mol}$$

kJ/mol

$$\ln K_p^{\circ} = - \frac{\Delta G_{1000}^{\circ}}{RT}$$

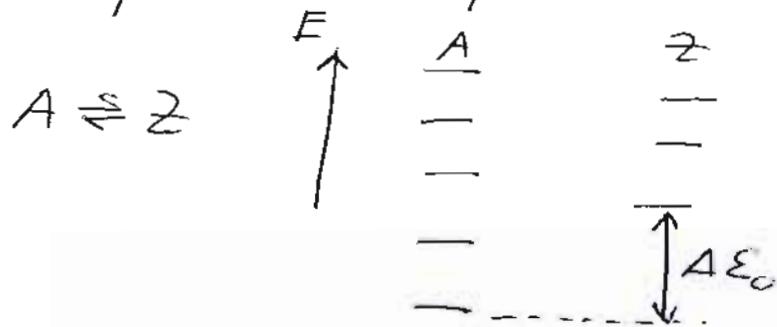
(44)-3

$$= 17,37$$

$$\rightarrow K_p = 2,9 \cdot 10^{-8} \text{ bar}^{-2}$$

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \cdot P_{\text{H}_2}^2} = \frac{\text{bar}}{\text{bar}^3}$$

from partition functions



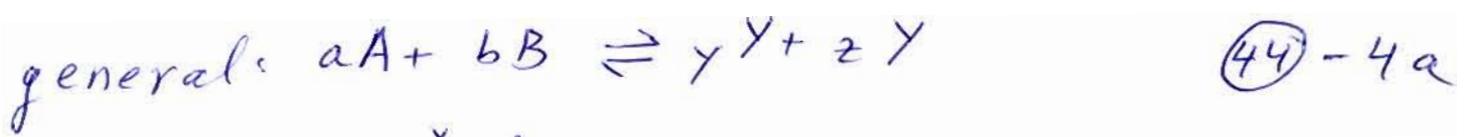
no other levels, only lowest ones!

$$K = \frac{[Z]}{[A]} = e^{-\Delta \varepsilon_0 / k_B T} \quad \text{if only lowest}$$

more levels: ratio of partition functions weighted

by $\Delta \varepsilon_0$

$$K = \frac{q_Z}{q_A} e^{-\Delta \varepsilon_0 / k_B T}$$



$$\rightarrow K = \frac{q^y q^z}{q_A^a q_B^b} e^{-\Delta E_0 / k_B T}$$

molecular equilibrium constant

if q is per unit volume

→ molar K_c from m^{-3}

$$\Delta G^\circ - U_0^\circ = -k_B T \ln Q + Nk_B T$$

(A at N_A dropped)

$$= -k_B T \ln \left(\frac{q_e}{N} \right)^N + Nk_B T \quad \text{for 1 comp.}$$

$$= -Nk_B T \ln \frac{q_e}{N} + Nk_B T$$

$$= -Nk_B T \ln \frac{q}{N} - Nk_B T (\ln e) + Nk_B T$$

$$= -RT \ln \frac{q}{N} ; G^\circ = U_0^\circ - RT \ln \frac{q}{N}$$

reactions

$$\Delta G^\circ = y G_y^\circ + z G_z^\circ - a G_A^\circ - b G_B^\circ$$

$$= y U_{0,y}^\circ + z U_{0,z}^\circ - a U_{0,A}^\circ - b U_{0,B}^\circ$$

$$- RT \ln \left[\frac{\left(\frac{q_y}{N} \right)^y \left(\frac{q_z}{N} \right)^z}{\left(\frac{q_A}{N} \right)^a \left(\frac{q_B}{N} \right)^b} \right]$$

$$\Delta G^\circ = \Delta U_0^\circ - RT \ln \left[\frac{\left(\frac{q_z}{N}\right)^2 \left(\frac{q_y}{N}\right)^y}{\left(\frac{q_A}{N}\right)^\alpha \left(\frac{q_B}{N}\right)^\beta} \right] \quad (44)-46$$

$$\sum v = y + z - \alpha - \beta$$

$$\Delta G^\circ = -RT \ln e^{-\frac{\Delta U_0^\circ}{RT}} - RT \ln \left[\frac{q_y^y q_z^z}{q_A^\alpha q_B^\beta} N^{-\sum v} \right]$$

$$\Delta G^\circ = -RT \ln \left\{ \frac{q_y^y q_z^z}{q_A^\alpha q_B^\beta} N^{-\sum v} e^{-\frac{\Delta U_0^\circ}{RT}} \right\}$$

$$\Delta G^\circ = -RT \ln K^\circ$$

$$\rightarrow K^\circ = \frac{q_y^y q_z^z}{q_A^\alpha q_B^\beta} N^{-\sum v} e^{-\frac{\Delta U_0^\circ}{RT}}$$

thermodynamic equilibrium constant
no dimension (unit)

practical: same value, unit having
mol/m³

K_c for $H_2 \rightleftharpoons 2H$

(44)-5

at 300K and at 3000K

H groundstate: $^2\Sigma_{1/2}$

next higher state negligible

$$D_0(H_2) = 431.8 \text{ kJ/mol}, \gamma_{HH} = 0.074 \text{ nm}$$

$$\theta_{vib}(H_2) = 6210 \text{ K}$$

$$K = \frac{q^2(H)}{q(H_2) N^{\sum_\nu}} e^{-\Delta U_0 / RT}$$

$$= \frac{1}{N} \frac{q^2(H_0)}{q(H_2)} e^{-\Delta U_0 / RT}$$

$$\sum_\nu = 2 - 1 = 1$$

Some contributions to the q -s

we will take from earlier,

examples

a) 300 K: $q_t(H) = 9.89 \cdot 10^{29}$ for 1 m^3

doublet groundstate $Q_e(H) = 2$

$\epsilon_0 = 0$ (defined)

$$\rightarrow q(H, 300K, 1m^3) = 2 \cdot q_t(H)$$

(44)-6

$$= 1.978 \cdot 10^{30}$$

$$q(H_2, 300K, 1m^3) = q_t q_r q_v q_e$$

$q_e = 1$: singlet \rightarrow 1 non-degenerate level

at $\varepsilon_c = 0$

$$q_t(H_2, 300K) = 2^{3/2} q_t(H, 300K)$$

↑

because $m_{H_2} = 2m_H$

$$= 2.797 \cdot 10^{30}$$

earlier we have determined:

$$q_r(H_2) = 1.707$$

$$q_v(H_2) = 1 \quad \text{from } \frac{1}{1 - e^{-\Theta_{vib}/k}}$$

$$\rightarrow q(H_2, 300K, 1m^3) = 4.78 \cdot 10^{30}$$

$$\rightarrow \text{at } 300K: K_c^o = \frac{q^2(H)}{q(H_2)N} e^{-\Delta U_0/kT}$$

$$\Delta U_0 = D_o(H_2)$$

$$N = N_A$$

→ dimensionless, thermodyn. (44)-7
 equilibrium constant at 300K, 1m^3

$$K_c^0 = 8.95 \cdot 10^{-70}$$

practical: $K_c = 8.95 \cdot 10^{-70} \frac{\text{mol}}{\text{m}^3}$

$$= 8.95 \cdot 10^{-70} \frac{\text{mol}}{\text{dm}^3}$$

K_c : same value as K_c^0 and if

K_c^0 was for 1m^3 , units are in $\frac{\text{mol}}{\text{m}^3}$

b) 3000 K: $q_t \sim T^{3/2}$ $q_r \sim T$

$$q_{\text{H}_2}(H, 3000\text{K}) = 10^{3/2} q(H, 300\text{K})$$

$$10 = \frac{3000\text{K}}{300\text{K}}$$

q_r does not exist for H

$$q(H, 3000\text{K}, 1\text{m}^3) = 6.255 \cdot 10^{31}$$

$$q_t(H_2, 3000\text{K}, 1\text{m}^3) = 10^{3/2} q_t(H_2, 300\text{K})$$

$$= 8.845 \cdot 10^{31}$$

$$q_r(H_2, 3000K, 1m^3) = 10q_r(H_2, 300K) \quad (44)-8$$

$$= 17.07$$

$$q_v(H_2, 3000K, 1m^3) = \frac{1}{1 - e^{-\theta_{vib}/3000K}}$$

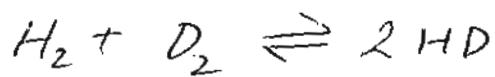
$$= 1.144$$

$$\rightarrow q(H_2, 3000K, 1m^3) = 1.727 \cdot 10^{33}$$

$$\rightarrow K_c^0 = 0.114$$

$$K_c = 0.114 \frac{\text{mol}}{\text{m}^3} = 1.14 \cdot 10^{-4} \frac{\text{mol}}{\text{dm}^3}$$

$\rightarrow H_2$ dissociation does not occur at 300K, but is quite appreciable at 3000K



$$m_H = 1.0078 \text{ amu} \quad m_D = 2.014 \text{ amu}$$

$$\overline{D}: H_2 \quad 4371 \text{ cm}^{-1} \quad D_2 \quad 3092 \text{ cm}^{-1}$$

$$HD \quad 3786 \text{ cm}^{-1}$$

$$\chi_c = 0.074 \text{ nm} \text{ for all}$$

$$K_c = ?$$

(44)-9

$$\Delta U_0 = \Delta \varepsilon_0$$

from zero-point energies

$$H_2: \frac{1}{2} \cancel{hc} \bar{\nu}_0 = 4,341 \cdot 10^{-20} \text{ J}$$

$$HD: \frac{1}{2} hc \bar{\nu}_0 = 3,760 \cdot 10^{-20} \text{ J}$$

$$D_2: \frac{1}{2} hc \bar{\nu}_0 = 3,071 \cdot 10^{-20} \text{ J}$$

$$\Delta \varepsilon_0 = [2 \cdot \varepsilon_0(HD) - \varepsilon_0(H_2) - \varepsilon_0(D_2)]$$

$$= 1,08 \cdot 10^{-21} \text{ J}$$

$$e^{-\Delta U_0 / RT} = e^{-\Delta \varepsilon_0 / k_B T} = e^{-0,2607} = 0,771$$

	m/kg	$I/\text{kg m}^2$
H_2	$3,345 \cdot 10^{-27}$	$4,583 \cdot 10^{-48}$
HD	$5,018 \cdot 10^{-27}$	$6,109 \cdot 10^{-48}$
D_2	$6,689 \cdot 10^{-27}$	$9,157 \cdot 10^{-48}$

$$\sum \nu = 0 \rightarrow N^{-\sum \nu} = N^0 = 1$$

$$K_c^\circ = \frac{q^2(HD)}{q(H_2)q(D_2)} e^{-\Delta U_0 / RT}$$

$$q = q_r \cdot q_t :$$

(44) - 10

$$q^2(HD) = \frac{(2\pi m_{HD} k_B T)^3}{h^6} \cdot \left(\frac{8\pi^2 I_{HD} k_B T}{\sigma_{HD} h^2} \right)^2$$

$$\sigma_{HD} = 1 \quad \sigma_{H_2} = \sigma_{D_2} = 2$$

$$K = \frac{m_{HD}^3}{(m_{H_2} m_{D_2})^{3/2}} \frac{I_{HD}^2}{I_{H_2} I_{D_2}} \frac{\sigma_{H_2} \sigma_{D_2}}{\sigma_{HD}^2} e^{-\Delta U_0 / RT}$$

$$= 3.26$$

not far from 4 : ratio of the

symmetry numbers $\frac{2 \cdot 2}{1}$

if equal amounts of H_2 and D_2

go to equilibrium :

each atom in a molecule has a chance of $\frac{1}{2}$ to be H and a chance of $\frac{1}{2}$ to be D

→ an AB molecule

(44)-11

has a chance to be H_2 :

$$\frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$$

has a chance to be D_2 :

$$\frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$$

chance to be HD : $\frac{1}{4}$

chance to be DH : $\frac{1}{4}$

→ chance to be HD : $\frac{1}{4} + \frac{1}{4} = \frac{1}{2}$

(both, HD and DH , included)

→ ratio $H_2 : HD : D_2 = \frac{1}{4} : \frac{1}{2} : \frac{1}{4} = 1 : 2 : 1$

$$\rightarrow \frac{[HD]^2}{[H_2][D_2]} \approx \frac{2^2}{1 \cdot 1} = 4$$

mass effects cancel out to a large part; almost

but because exponential that is

$$e^{-\frac{\Delta U_0}{RT}} = 0.771 : 4 \approx 3.26$$

Transition State Theory

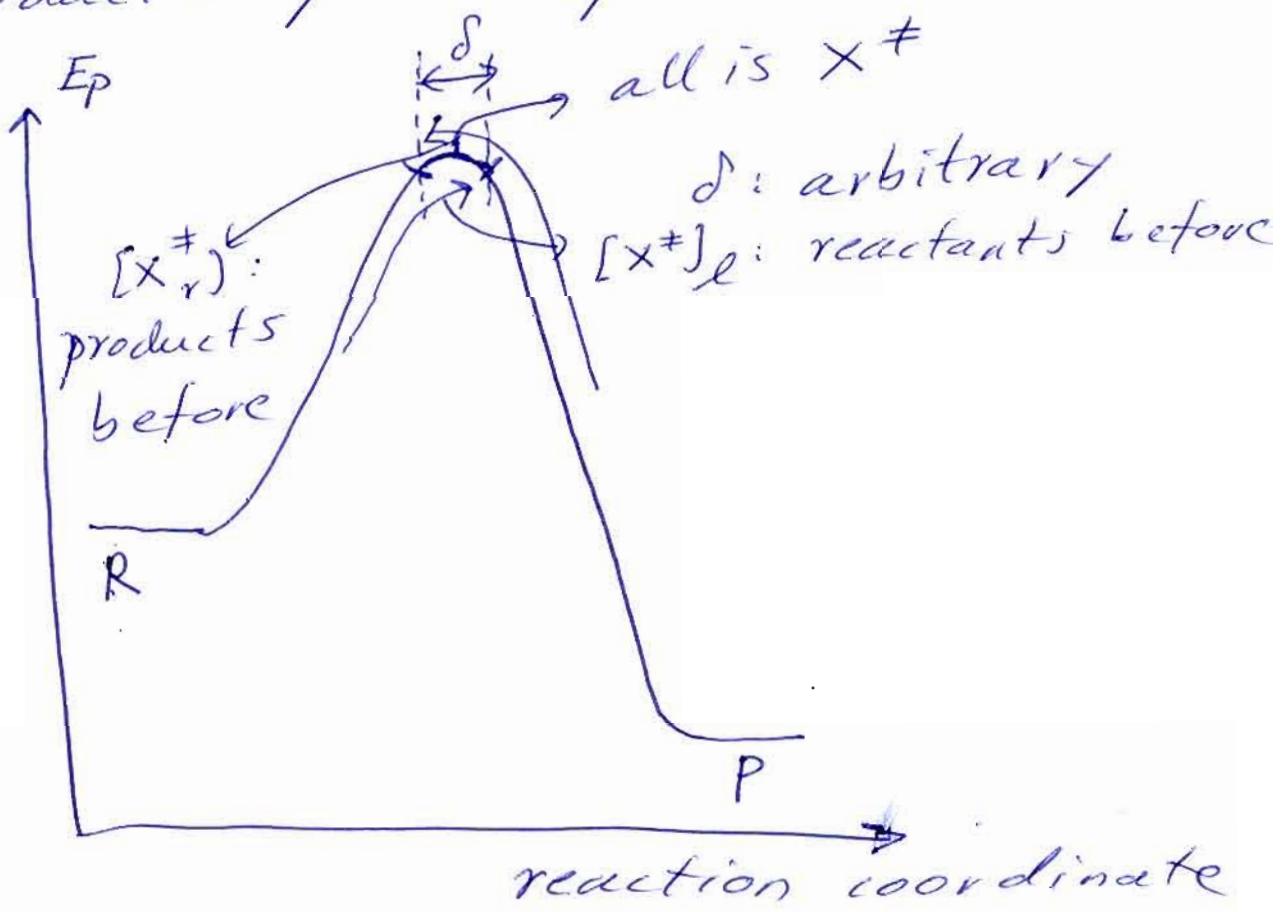
(1)

Sec. 9.9 TST not derived but
made plausible (believable)

by thermodynamic analogies to
real equilibrium

most important assumption

activated complexes X^* formed
in equilibrium with reactants and
products: quasi-equilibrium



δ : makes no difference how large is δ

example reactions



(2)

ideal behavior assumed

complete equilibrium is reached

$$\Rightarrow K_c = \left(\frac{[X^+]}{[A][B]} \right)_{eq} \text{ formation of } X^+ \text{ from reactants}$$

K_c from partition functions

q^+ complete partition function of activated complex

$$\left(\frac{[X^+]}{[A][B]} \right)_{eq} = K_c = \frac{q^+}{q_A q_B} e^{-\frac{E_0}{RT}}$$

E_0 : difference of molar 0-point energies ε_m°

$$E_0 = \varepsilon_m^\circ (X^+) - \varepsilon_m^\circ (A) - \varepsilon_m^\circ (B)$$

→ q -s must be developed with respect to the 0-point levels of molecules

$$\Rightarrow [X^+] = [A][B] \frac{q^+}{q_A q_B} e^{-\frac{E_0}{RT}}$$

$\backslash / /$
equilibrium values

Activated complexes X^+ all the same, but of 2 types:

X_e^+ : formed in the immediate past from reactants $A + B \xrightarrow{k_1} X_e^+$ (3)

X_r^+ : formed in the immediate past from products: $Y + Z \xrightarrow{k_{-1}} X_r^+$

$$[X^+] = [X_e^+] + [X_r^+]$$

because equilibrium: $v_i = v_{-i}$

$$\Rightarrow [X_e^+] = [X_r^+] = \frac{1}{2}[X^+]$$

$$\rightarrow [X_e^+] = \frac{1}{2}(A)(B) \frac{q^+}{q_A q_B} e^{-E_0/RT}$$

so far's everything in complete equilibrium

imagine to remove all product Y and Z

then $[X_r^+] = 0$ because no more Y and Z to form X_r^+

but $[X_e^+]$ remains same because stating that the activated complexes are in equilibrium with

stating that the activated complexes are in equilibrium with the reactants, one means only the X_e^+ complexes formed from A and B in immediate past.

→ quasi-equilibrium

g[#]: for activated complex X^+

N_a atoms in A

N_b atoms in B

→ X^+ contains $N_a + N_b$ atoms

3 translational degrees of freedom

- if X^+ non-linear molecule:

3 rotational deg. of freedom

→ $3(N_a + N_b) - 6$ vibrational freedoms

1 vibration is special:

the one passing over the maximum of the E_p curve:

special: no restoring force (maximum)

factor in q^{\neq} for 1 vibration:

$$\frac{1}{1 - e^{-\frac{h\nu}{k_B T}}}$$

(5)

but for a passage over a maximum
of E_p (no restoring force): $\nu \rightarrow 0$

X^+ passes over the maximum without
constraint into products:

expand exponential, keep only up
to linear term in ν :

$$\lim_{\nu \rightarrow 0} \frac{1}{1 - e^{-\frac{h\nu}{k_B T}}} = \frac{1}{1 - (1 - \frac{h\nu}{k_B T})} = \frac{k_B T}{h\nu}$$

\rightarrow complete partition function
 q^{\neq} of X^+ :

$$q^{\neq} = q_{\neq} \frac{k_B T}{h\nu}$$

q_{\neq} partition function of X^+
without the special $\nu \rightarrow 0$ vibration:

$$\text{in } q_{\neq} \begin{cases} 3(N_a + N_b) - 7 \text{ vibrations if } X^+ \text{ non-linear} \\ 3(N_a + N_b) - 6 \quad " \quad \text{if } X^+ \text{ linear} \end{cases}$$

$$\rightarrow [X^+] = [A][B] \frac{k_B T}{h\nu} \frac{q_A q_B}{q_A' q_B'} e^{-E_0/RT}$$

if ν is a normal vibration of a usual bond (the $\nu \rightarrow 0$ case over maximum) then it would be $\nu = \frac{1}{T}$
 T: time for the bond to make a complete vibration from x_{\max} to $-x_{\max}$ and back to x_{\max}

for the special vibration ν is $1/(time \text{ to travel } \underline{\text{twice}} \text{ through } \delta)$

for reaction rate $k=k_1$: consider time to pass through δ once: t_δ

thus frequency is $\frac{1}{t_\delta} = 2\nu$

cause $\nu = \frac{1}{2t_\delta}$

v.: rate of reaction from reactants:
 $v = [X_e^+]/t_p$ time to make the trip through δ once to the products

$$\rightarrow v = 2\nu [X_e^+] \quad [X_e^+] = \frac{1}{2} [X^+]$$

$$= 2\nu \frac{1}{2} [X^+] = \nu [X^+]$$

(7)

$$\rightarrow v = (A][B] \frac{k_B T}{h} \frac{q^+}{q_A q_B} e^{-E_0/RT}$$

ν cancels!

by definition: $v = k[A][B]$

$$\Rightarrow \boxed{k = \frac{k_B T}{h} \frac{q^+}{q_A q_B} e^{-E_0/RT}}$$

Eyring equation

important to realize:

$$[X_e^+] = [X_r^+] = \frac{1}{2} [X^+]$$

ν : frequency for travelling
through δ twice

but needed here: trip through
 δ once without return trip,
directly to products!

example



(8)

at 300 K, given:

barrier height E_b from zero-point level: $E_b = 5.0 \text{ kJ/mol}$

$$R_{H-Br} = 141.4 \text{ pm} \quad \nu_{H-Br} = 2650 \text{ cm}^{-1}$$

~~$R_{H-H} = 150 \text{ pm}$~~

X^\ddagger is $H \cdots H \cdots Br$, linear with

$$\text{with } R_{H-H} = 150 \text{ pm}, R_{H-Br} = 142 \text{ pm}$$

$$\nu(\text{symm. stretch}) = 2340 \text{ cm}^{-1} = \nu_s$$

$$\nu(\text{degenerate bendings}) = 460 \text{ cm}^{-1} = \nu_B$$

ν_4 of X^\ddagger is passage over maximum

q_H : q_H at 300 K was calculated before to be

$$q_H = 9.89 \cdot 10^{29} \text{ m}^{-3}$$

q_{HBr} : for ~~rotation~~ translation first

$$m_{Br} = \frac{79.90 \cdot 10^{-3} \text{ kg/mol}}{6.022 \cdot 10^{23} / \text{mol}} = 1.327 \cdot 10^{-25} \text{ kg}$$

translational partition function:

$$q_{t,HBr} = \frac{[2\pi(m_H + m_{Br})k_B T]^{3/2}}{h^3} \quad (9)$$

$$m_H = \frac{1.008 \cdot 10^{-3} \text{ kg/mol}}{N_A} = 1.674 \cdot 10^{-27} \text{ kg}$$

proton mass

$$\rightarrow q_{t,HBr} = 7.10 \cdot 10^{32} \text{ m}^{-3}$$

rotational moment of inertia

$$I = \mu R_{HBr}^2 = \frac{m_H m_{Br}}{m_H + m_{Br}} R_{HBr}^2$$

$$I = \frac{1.674 \cdot 10^{-27} \text{ kg} \cdot 1.327 \cdot 10^{-25} \text{ kg}}{(1.674 + 132.7) \cdot 10^{-27} \text{ kg}} \cdot (1.414 \cdot 10^{-10})^2 \text{ m}^2$$

$$= 3.305 \cdot 10^{-47} \text{ kg m}^2$$

$$q_{r,HBr} = \frac{8\pi^2 I k_B T}{h^2} = 24.6$$

$$q_{v,HBr} = \frac{1}{1 - e^{-\frac{h\nu}{k_B T}}} \quad \text{only 1 vibration}$$

$$\bar{\nu} = 2650 \text{ cm}^{-1} \quad \nu = \bar{\nu} c = 7.94 \cdot 10^{13} \text{ s}^{-1}$$

$$\frac{h\nu}{k_B T} = \frac{6.626 \cdot 10^{-34} \text{ Js} \cdot 7.94 \cdot 10^{13} \text{ s}^{-1}}{1.381 \cdot 10^{-23} \text{ J/K} \cdot 300 \text{ K}} = 12.7$$

$$\rightarrow q_{V,HBr} = \frac{1}{1 - e^{-12.7}} = 1 \\ (1.00000305)$$

(10)

$$\rightarrow q_{HBr} = 7.10 \cdot 10^{32} m^{-3} \cdot 24.6 \cdot 1 \\ = 1.75 \cdot 10^{34} m^{-3}$$

HBr^+ activated complex

$$m_{X^+} = 2m_H + m_{Br} = 1.37 \cdot 10^{-25} kg$$

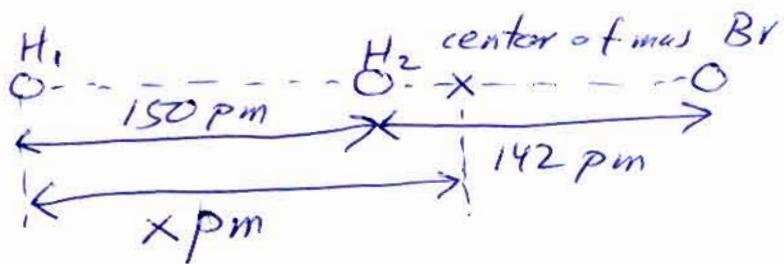
$$q_{t,X^+} = \frac{(\sqrt{2\pi m_{X^+} k_B T})^3}{h^3} \text{ power } 3/2$$

$$= \frac{(2\pi \cdot 1.37 \cdot 10^{-25} kg \cdot 1.381 \cdot 10^{-23} \frac{J}{kgK} \cdot 300K)^{3/2}}{(6.626 \cdot 10^{-34} Js)^3}$$

$$= 7.32 \cdot 10^{-32} m^{-3}$$

$$1 \frac{J^{3/2} kg^{3/2}}{J^3 s^3} = 1 \frac{kg^{3/2}}{J^{3/2} s^3} = 1 \frac{kg^{3/2}}{\frac{kg^{3/2} m^3}{s^3} s^3} = 1 m^{-3}$$

x_{pm} : distance of center of mass to terminal H atom



center of mass : c

$$m_H R_{H_1-C} + m_H R_{H_2-C} - m_{Br} R_{C-Br} = 0 \quad (11)$$

$$\begin{aligned} m_H x_{\cancel{pm}} + m_H (x - 150) pm &= m_{Br} (R_{H_1-Br} - x) pm \\ &\quad \downarrow \\ &(150 + 142) pm \\ &= 292 pm \end{aligned}$$

$$m_H [x_{\cancel{pm}} + x - 150] = m_{Br} (292 - x)$$

$$2m_H x + m_{Br} x = 292 m_{Br} + 150 m_H$$

$$x = \frac{292 m_{Br} + 150 m_H}{2m_H + m_{Br}} = 283.3$$

moment of inertia I_{X^+}

$$I = \sum_i m_i r_i^2$$

r_i distance from center of mass to atom i

$$\begin{aligned} I &= m_H (283.3 \cdot 10^{-12} m)^2 \\ &+ m_H [(283.3 - 150) \cdot 10^{-12} m]^2 \\ &+ m_{Br} [(292 - 283.3) \cdot 10^{-12} m]^2 \end{aligned}$$

$$I = m_H \left(283,3 \cdot 10^{-12} \text{ m}\right)^2 + m_H \left(133,3 \cdot 10^{-12} \text{ m}\right)^2$$

(12)

$$+ m_{Br} \left(8,7 \cdot 10^{-12} \text{ m}\right)^2 = 1,74 \cdot 10^{-46} \text{ kg m}^2$$

$$q_{r,x^\pm}^* = \frac{8\pi^2 \cdot I \cdot k_B T}{h^2}$$

$$= \frac{8\pi^2 \cdot 1,74 \cdot 10^{-46} \text{ kg m}^2 \cdot 1,381 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \cdot 300 \text{ K}}{(6,626 \cdot 10^{-34} \text{ Js})^2}$$

$$= 129,7 \cdot \frac{\text{J kg m}^2}{\text{J}^2 \text{s}^2} = 129,7 \frac{\text{J}^2}{\text{J}^2} = 129,7$$

$$q_{v,x^\pm}^* = \frac{1}{(1 - e^{-hv_s/k_B T})(1 - e^{-hv_B/k_B T})^2}$$

↳ only the 3 real vibrations included 2 degenerate bendings

$$\bar{\nu}_s = 2340 \text{ cm}^{-1}; \nu_s = c \cdot \bar{\nu}_s = 7,013 \cdot 10^{13} \text{ s}^{-1}$$

$$\bar{\nu}_B = 460 \text{ cm}^{-1}; \nu_B = c \cdot \bar{\nu}_B = 1,37 \cdot 10^{13} \text{ s}^{-1}$$

$$q_{v,x^\pm}^* = \frac{1}{(1 - e^{-11,2})(1 - e^{-2,19})^2} = 1,27$$

$$q_\pm^* = 7,32 \cdot 10^{32} \text{ m}^{-3} \cdot 129,7 \cdot 1,27 \\ = 1,21 \cdot 10^{35} \text{ m}^{-3}$$

$$k = \frac{k_B T}{h} \frac{q_+ q_{HBr}}{q_H q_{HBr}} e^{-E_0/RT}$$

(13)

E_0 given

$$k = \frac{1,381 \cdot 10^{-23} \frac{J}{K} \cdot 300 K \cdot 1,21 \cdot 10^{35} m^{-3}}{6,626 \cdot 10^{-34} J s \cdot 9,89 \cdot 10^{29} m^{-3} \cdot 1,75 \cdot 10^{39} m^{-3}}$$

$$\cdot \exp \left[-\frac{5000 \frac{J/mol}{K/mol} \cdot 300 K}{8,3145 \frac{J}{K mol}} \right]$$

$$= 4,367 \cdot 10^{-17} \frac{J}{J s m^{-3}} \cdot e^{-2,004}$$

$$= 4,367 \cdot 10^{-17} m^3 s^{-1} \cdot 0,1347$$

$$= 5,88 \cdot 10^{-18} m^3 s^{-1}$$

molecular units!

To obtain k in molar units ($M^{-1}s^{-1}$)

$$k \cdot N_A \cdot 1000 \frac{dm^3}{m^3} = k$$

$$\rightarrow k = 3,54 \cdot 10^9 M^{-1}s^{-1}$$

$$\text{Arrhenius: } k = A e^{-\frac{E_0}{RT}}; A = k e^{\frac{E_0}{RT}}$$

$$\rightarrow A = 2,63 \cdot 10^{10} M^{-1}s^{-1}$$

in thermodynamic functions:

$$k = \frac{k_B T}{h} e^{-\Delta^{\ddagger} G^\circ / RT}$$
$$= \frac{k_B T}{h} e^{\Delta^{\ddagger} S^\circ / R} e^{-\Delta^{\ddagger} H^\circ / RT}$$

(14)

here: $k = \frac{k_B T}{h} \frac{q_+}{q_A q_B} e^{-E_0 / RT}$

here q_+ is involved while in
the above one q^\ddagger is involved (K_c)

modified: $K_c^\ddagger = \frac{q_+}{q_A q_B} e^{-E_0 / RT}$

$$\rightarrow k = \frac{k_B T}{h} K_c^\ddagger$$

express K_c^\ddagger in terms of $\Delta^{\ddagger} G^\circ$, $\Delta^{\ddagger} H^\circ$ and $\Delta^{\ddagger} S^\circ$

→ above equ. from
Section 9.9

Improvements

(15)

call for large calculations

- some potential curves (shallow product minimum, not much below χ^{\ddagger}):

χ^{\ddagger} can bounce back to reactants after passing:

transmission coefficient:

ratio of attempts forming products over all attempts

- tunneling through maximum for light reactants

best for that: maximum not too high and barrier narrow (small δ)

for light H atoms and e⁻-transfer reactions important.

theory not worked out well

indication e.g. & unexpectedly large $V(H)/V(D)$ ratios

Way to equilibrium

(16)

1872 paper by Boltzmann:

before: approach to equil. qualitatively:

1) following Kelvin:

by dissipation of energy

2) following Clausius:

by increase of entropy in system +
surrounding in spontaneous processes

Boltzmann: quantitative derivation of
his H-function: $H \sim -S$

→ S must increase, thus H must
decrease in spontaneous processes
(for system + surroundings)

Boltzmann's claim: use of only
mechanical arguments on dynamics,
no use of probability

2 major objections to Boltzmann's
H theorem:

1) Kelvin in 1874:

reversibility argument:

(17)

system like a gas goes from a non-equilibrium to its equilibrium state then H must decrease

But, since the argument is purely mechanical, all molecular motions can be reversed

→ then process away from equilibrium with H increasing

possible in mechanics → H increase possible

Boltzmann (1877):

large number of equil. states exist

but when initial state is specified

→ just one equilibrium state can come out

→ probability tells that motion to equil. is far more probable than away from it

transition with H increase very unlikely.

(18)

But now probability is involved

2) Poincaré:

recurrence paradox

any system, like a gas, driven purely by mechanics must reach any possible configuration in time

\Rightarrow system can reach any state

$\Rightarrow H$ cannot always decrease

Boltzmann's H theorem can be violated, but that is highly unlikely and would need infinite time to occur

again probability in

Boltzmann had probability in H from the beginning, by neglecting unlikely collisions between particles.

however, his H theory lead to understand the way to equil.,
but is not purely mechanical

(19)

second law is a matter of probability,
but by a chance almost always certain

Boltzmann:

W : number of ways (possible ones) to realize a given distribution of states

then $S = k_B \log W$

from this all thermodynamic functions can be calculated

this definition includes naturally informational entropy

entropy changes when mixing two gases different,

whether the information is:

the gases are identical

the gases are different

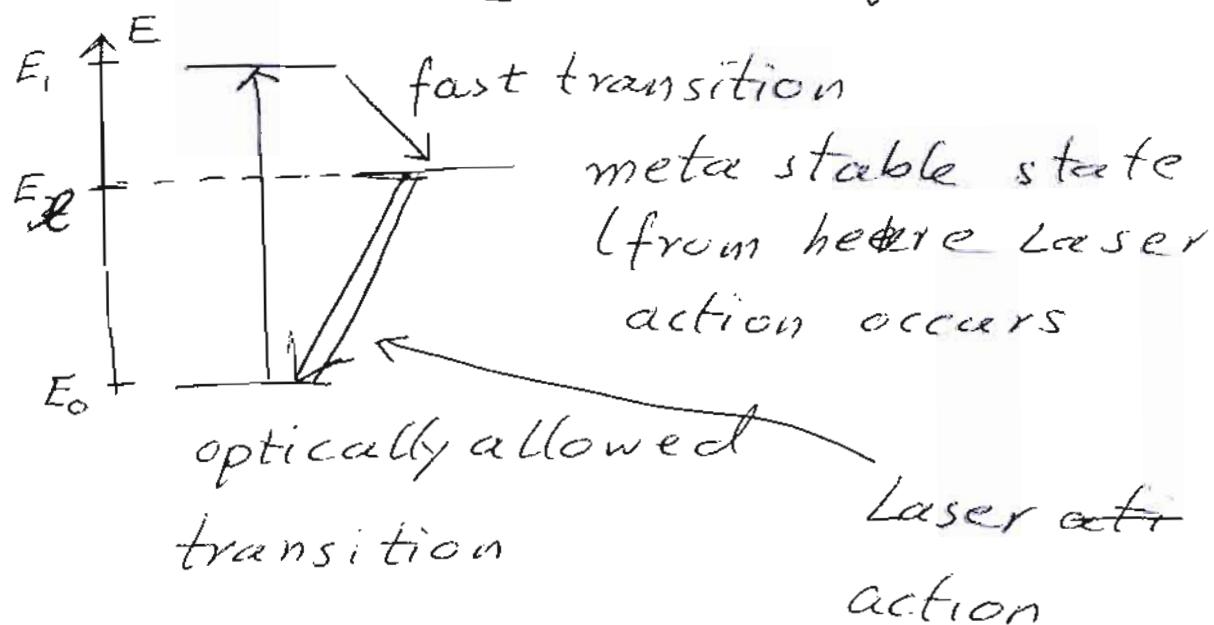
See 15.10 out not needed

reviewchap. 14

for Laser function necessary:

- 1) Population inversion
- 2) Emitted photons must stimulate further emission (mirrors in cavity)
- 3) Excited state must be metastable (long life time \rightarrow pop. inversion)

3-state Laser (ruby e.g.)



$$\Delta E = E_\ell - E_0$$

Laser light: $\nu = \frac{\Delta E}{h}$

$$\tilde{\nu} = \frac{\Delta E}{hc} \quad \text{if } E\text{-s in cm}^{-1}$$

then $\Delta E = \tilde{\nu}$

$$\lambda = \frac{c}{\nu} = \frac{ch}{\Delta E}$$

- emitting state must be:

- 1) metastable

- 2) state E_ℓ must decay to E_ℓ
not to E_0

frequency doubling: piezo electric crystals

- induced polarization:

$$P = \beta_1 E + \beta_2 E^2 \dots$$

non linear effect!

Light: $E = E_0 \sin 2\pi\nu_0 t$

$$\rightarrow P^{(2)} = \beta_2 E_0^2 \sin^2 2\pi\nu_0 t \neq$$

$$= \frac{1}{2} \beta_2 E_0^2 (1 - \cos 4\pi\nu_0 t)$$

↓ static ↗ double frequency

line widths

Doppler effect: $v' = \left[1 \pm \frac{u}{c}\right] v$

$$\Delta v = \pm \frac{u}{c} v$$

→ Gaussian curve of the line shape:

$I(v)$ intensity

because of movement of molecules

width at half height:

$$\Delta v_1 = 2 \left(\frac{d}{c}\right) \sqrt{\frac{2k_B T}{m}}$$

Lifetime broadening

Uncertainty principle:

$$\Delta E \Delta \tau \geq (\approx) \frac{\hbar}{2} \quad \hbar = \frac{h}{2\pi}$$

$$\Delta \bar{v} (\text{cm}^{-1}) = \frac{2.7 \cdot 10^{-12}}{\Delta \tau / \text{s}}$$

$$\Delta E = \frac{\hbar}{2\Delta \tau} \rightarrow \Delta \bar{v} = \frac{\Delta E}{\hbar c}$$

$$\Delta \bar{v} = \frac{\hbar/2\pi}{2\Delta \tau \hbar c} = \frac{1}{4\pi \Delta \tau c}$$

Mössbauer spectroscopy

γ -rays : frequency about

$$\nu = 3.5 \cdot 10^{18} \text{ Hz}$$

a) emission by free ^{57}Fe atom

b) " by ^{57}Fe atoms in a lg crystal

c) frequency shift when the crystal moves with a speed v

$\frac{h\nu}{c} = m_e v$ recoil for momentum conservation when $h\nu$ is emitted

energy: $\Delta E = h\nu = 2.32 \cdot 10^{-15} \text{ J}$
of a photon of $3.5 \cdot 10^{18} \text{ Hz}$

a) $\frac{h\nu}{c} = m_e v \Rightarrow v = \frac{h\nu}{c \cdot m_{\text{Fe}}}$

$$m_{\text{Fe}} = \frac{57 \cdot 10^{-3} \text{ kg/mol}}{N_A} \rightarrow v$$

$\rightarrow \Delta v = \frac{v}{c} v$ frequency change by recoil of a free Fe atom

6) if Fe is in a crystal, then
the whole crystal recoils when
photon is emitted

$$\rightarrow u = \frac{h\nu}{cm} \xrightarrow{\text{Crystal}} ig$$

$$\rightarrow \Delta v = \frac{u}{c} v$$

a much smaller

→ γ -line much sharper

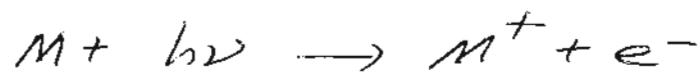
c) crystal moves with speed u :

frequency change?

$$\Delta V = \frac{U_{\text{crystall}}}{C} \Delta T$$

Photoelectron spectroscopy

photo electric effect



by UV or X-rays

conservation of energy

$$E(M) + h\nu = E(\text{K}^+) + E_K(e^-)$$

ionization potential IP

$$IP = E(M^+) - E(M) = h\nu - E_k(e^-)$$

plot: rate of electron emission

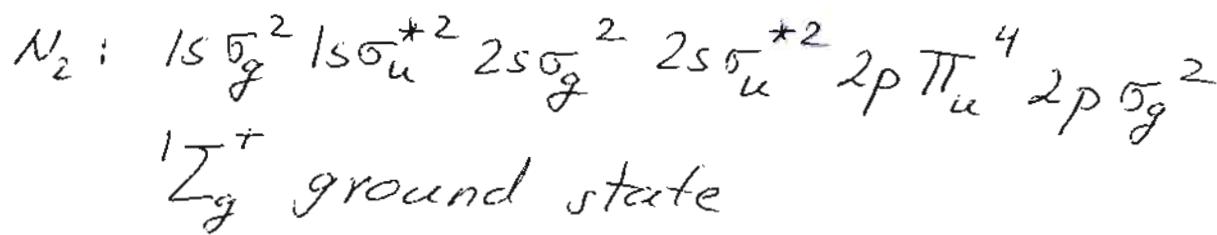
vs. $E_k(e^-)$

or vs. ionization energy

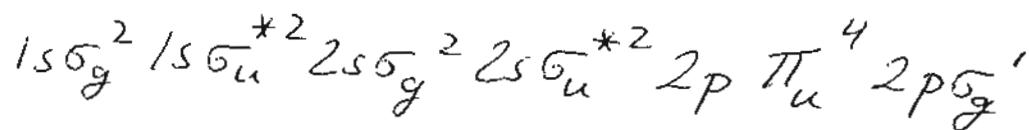
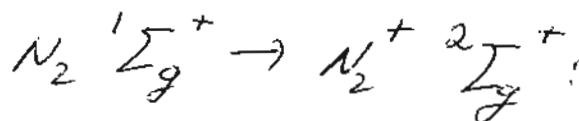
in the book as example a spectrum
is shown:

3 groups of lines, origin?

spectrum of N_2



2 lines with smallest ionization energy,



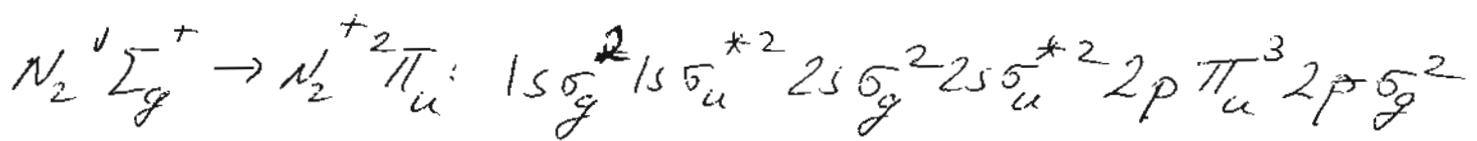
group of 2 lines because transition
can occur into different vibrational
levels of N_2^+

ground state: almost only $v=0$
populated

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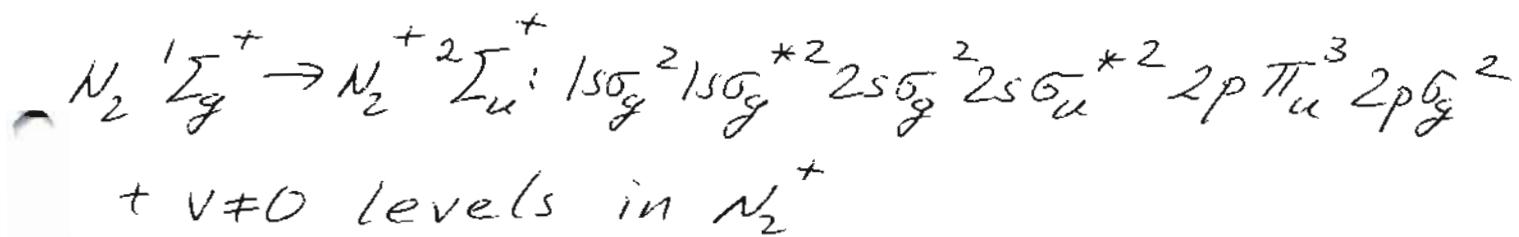
next group of lines intermediate

IP:



again $v \neq 0$ vibr. levels of N_2^+
involved in the group of lines

highest IP:



Chiroptical methods

Nature of polarized light was
discussed and also methods to
generate polarized light

optical activity

plane of polarized light is rotated
at optically active centers in sample

α' : optical rotation

n_L, n_R different refractive indices for
left (L) and right (R) circular
polarized light

$$\rightarrow \alpha' = \frac{\pi}{\lambda} (n_L - n_R)$$

light path length

rotation angle: $\alpha = \alpha' d$

specific rotation:

$$[\alpha]_A = \frac{\alpha}{cl}$$

l : light path length

c : concentration

Chap. 15molecular statistics

$3N_a$ degrees of freedom when a molecule has N_a atoms (x_1, y_1, z for each atom)

linear molecules:

- 3 translations + 2 rotations of the molecule as a whole:
 $\rightarrow 3N_a - 5$ vibrations

non linear molecules:

- 3 translations + 3 rotations of the molecule as a whole:
 $\rightarrow 3N_a - 6$ vibrations

contribution of $\frac{1}{2}k_B T$ for each translation and rotation
and of $k_B T$ for each vibration
to the average internal energy

molar internal energy U_m

$$3 \text{ translations: } U_m = \frac{3}{2} RT$$

$$C_{V,m} = \left. \frac{dU}{dT} \right|_V \rightarrow \frac{C_{V,m}}{R} = \frac{3}{2}$$

this classical concept of equipartition of energy over all states

is well fulfilled ideal monatomic gases like He, Ne, Ar, -

which have only translations and translational levels are very close in energy

for rotations - also densely spaced levels compared to $k_B T$ - the agreement equipartition - experiment not 100% but not too bad

but the agreement is not good at all for vibrations

→ no equipartition of energy
for widely spaced levels

Boltzmann distribution:

$$\frac{n_i}{N} = \frac{e^{-\epsilon_i/k_B T}}{q}$$

molecular partition function q

for non-degenerate levels:

$$q = \sum_i e^{-\epsilon_i/k_B T}$$

for g_i -times degenerate levels ϵ_i :

$$q = \sum_i g_i e^{-\epsilon_i/k_B T}$$

system partition function: Q

countable molecules (crystal):

$$Q = q^N$$

indistinguishable molecules (gas):

$$Q = \left(\frac{q^N}{N!}\right)^N$$

example:

$$Q = \left(q_{\text{transl.}} \cdot q_{\text{rot.}} \cdot q_{\text{vib.}} \cdot q_{\text{el.}} \cdot q_{\text{nuc.}} \cdot \frac{e}{N} \right)^N$$

$\left(\frac{e}{N}\right)^N$ must be included only in one of the factors, usually in $q_{\text{transl.}}$.

$$q_{\text{transl.}} = \left(\frac{q_{\text{transl.}} e}{N} \right)^N$$

for the other factors e.g. rot.
then

$$q_{\text{rot.}} = q_{\text{rot.}}^N \text{ sufficient}$$

inner energy

$$U - U_0 = k_B T^2 \left. \frac{\partial \ln Q}{\partial T} \right|_V \rightarrow \text{volume}$$

U_0 (at 0K) can mostly be set to 0

entropy:

$$S = \frac{U - U_0}{T} + k_B \ln Q$$

Helm holtz energy:

$$A - U_0 = -k_B T \ln Q$$

Pressure

$$P = k_B T \left. \frac{\partial \ln Q}{\partial V} \right|_T$$

ideal gas:

$$PV = Nk_B T (= nRT)$$

enthalpy

$$H - U_0 = U + PV = k_B T^2 \left. \frac{\partial \ln Q}{\partial T} \right|_V + Nk_B T$$

for ideal gas

Gibbs energy

$$G - U_0 = -k_B T \ln Q + Nk_B T$$

(ideal gas)

$$Q = q_t \cdot q_r \cdot q_v \cdot q_e \cdot q_n$$

↑
nuclei

translation

for ideal monatomic gases:

$$\frac{q_t}{t} = \frac{(2\pi m k_B T)^{3/2} V}{h^3} = \text{const. } T^{3/2} V$$

$$\ln Q = \ln \left(\frac{q_t e}{N} \right)^N$$

$$= N \ln \left[\text{const. } \frac{T^{3/2} V}{N} \right] + N$$

↑
from $\ln e^n = n$

$$\rightarrow U = k_B T^2 \left. \frac{\partial \ln Q}{\partial T} \right|_V = \frac{3}{2} N k_B T$$

enthalpy

$$H = U + PV = \underbrace{\frac{3}{2} N k_B T}_U + \underbrace{N k_B T}_{PV}$$

for ideal gas

$$= \frac{5}{2} N k_B T$$

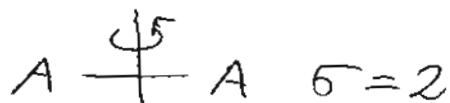
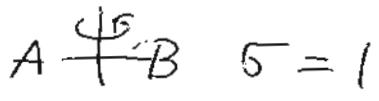
heat for T increase by ΔT at constant pressure:

$$\text{heat} = \Delta H = \frac{5}{2} N k_B T$$

rotations

$$q_r = \frac{8\pi^2 I k_B T}{5h^2} \quad \text{linear molecules}$$

σ : symmetry number

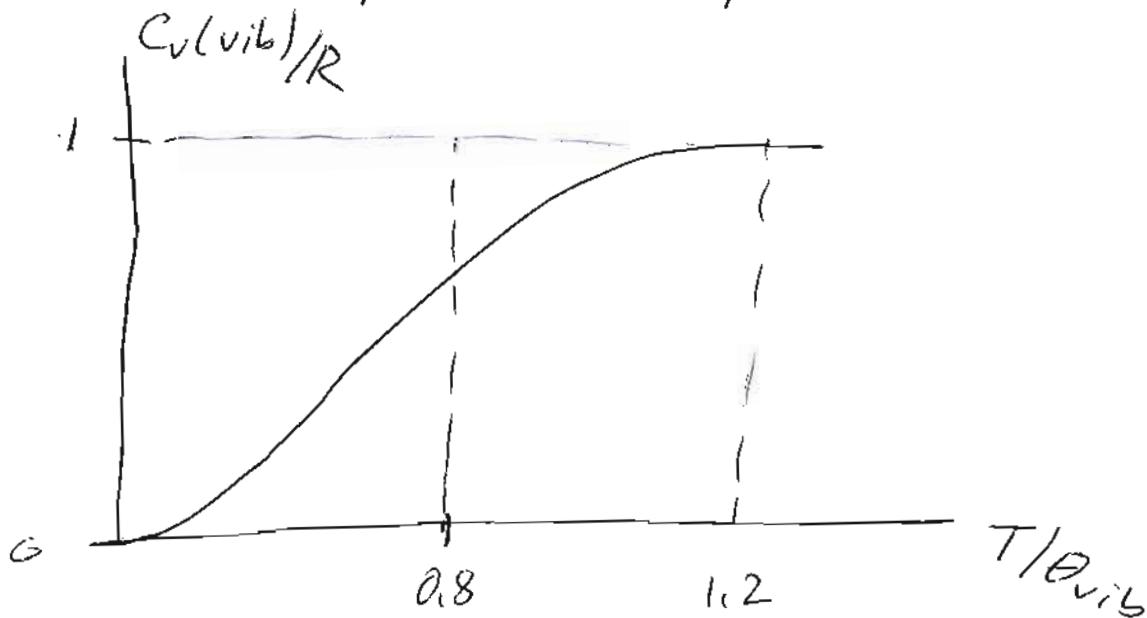
vibrations

factor $q_v = \frac{1}{1 - e^{-\theta_{vib}/k_B T}} \quad \theta_{vib} = \frac{h\nu}{k_B}$

for each vibration (normal mode)

$$\frac{C_v(\text{vib})}{R} = \left(\frac{\theta_{vib}}{T} \right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T} - 1)^2}$$

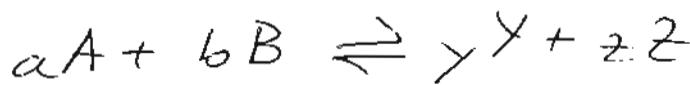
Einstein function for 1 vibration



electronic

only a few states must be included

mostly q_e very close to 1

equilibrium constants

$$K^{\circ} = \frac{q_Y^y q_Z^z}{q_A^a q_B^b} N^{-\sum_v} e^{-\frac{\Delta U_0}{RT}}$$

$$\Delta U_0 = yU_0(Y) + zU_0(Z) - aU_0(A) - bU_0(B)$$

(per mol) $\stackrel{\uparrow}{\text{Σ}_v}$ levels

$$\sum_v = y+z-a-b$$

H_2 : ground state ${}^2\Sigma_{1/2}$

higher electronic states negligible

$$D_0(H_2) = 431.8 \text{ kJ/mol}$$

$$\gamma_{H_2} = 0.074 \text{ nm}$$

$$\theta_{\text{vib}} = 6210 \text{ K}$$

(45) 17

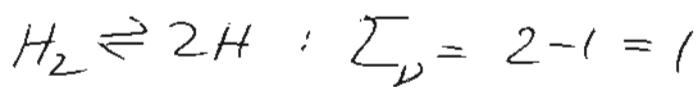
known from earlier calculation:

$$q_t(H, 300K) = 9.89 \cdot 10^{29} \text{ for } 1m^3$$

$$q_r(H_2, 300K) = 1.707$$

$$q_v(H_2, 300K) = 1$$

K for dissociation $H_2 \rightleftharpoons 2H$ at 300K
and 3000K for $1m^3$?



$$\begin{aligned} K &= \frac{q^2(H)}{q(H_2)} N^{-\sum_{\nu}} e^{-\Delta U_0 / RT} \\ &= \frac{1}{N} \frac{q^2(H)}{q(H_2)} e^{-\Delta U_0 / RT} \end{aligned}$$

a) 300K: doublet ground state in H

$$\rightarrow q_e(H) = 2$$

doublet : 2 fold degeneracy
of $\varepsilon_0 = 0$

$$\begin{aligned} \rightarrow q(H, 300K, 1m^3) &= 2q_t(H, 300K) \\ &= 1.978 \cdot 10^{30} \end{aligned}$$

no rot. / vib.

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$$q(H_2, 300K, 1m^3) = q_t q_r q_v q_e$$

$q_e = 1$ (singlet ground state only)

$$q_t(H_2, 300K) = 2^{3/2} q_t(H, 300K)$$

$$\hookrightarrow q \sim m^{3/2} \text{ and } m_{H_2} = 2m_H$$

→ with the data from before:

$$\begin{aligned} q(H_2, 300K, 1m^3) &= q_t(H_2) q_r(H_2) q_v(H_2) q_e(H_2) \\ &= 4,78 \cdot 10^{30} \end{aligned}$$

$$\rightarrow K_{300K}^o = 8,95 \cdot 10^{-70}$$

$$\text{practical: } K_{300K} = 8,95 \cdot 10^{-70} \frac{\text{mol}}{\text{m}^3}$$

→ H_2 dissociation is negligible at 300K

$$\text{b) } 3000K: q_t \sim T^{3/2}$$

$$\rightarrow q_t(3000K) = \left(\frac{3000}{300}\right)^{3/2} q_t(300K)$$

$$q_r \sim T$$

$$\rightarrow q_r(3000K) = \frac{3000}{300} q_r(300K)$$

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$$q(H_1, 3000K) = 10^{3/2} q(H_1, 300K)$$

$$= 6.255 \cdot 10^{31}$$

$$(q(H) = q_t(H) \cdot q_e(H) = 2q_t(H))$$

$$q_t(H_2, 3000K) = 10^{3/2} q_t(H_2, 300K)$$

$$= 8.845 \cdot 10^{31}$$

$$q_r(H_2, 3000K) = 10 q_r(H_2, 300K)$$

$$= 17.07$$

$$\rightarrow \cancel{q(H_2, 3000K)}$$

$$q_v(H_2, 3000K) = \frac{1}{1 - e^{-\theta_{vib}/3000K}} = 1.144$$

$$\rightarrow q(H_2, 3000K) = 1.727 \cdot 10^{33} (q_e = 1)$$

$$\rightarrow K_{3000K}^{\circ} = 0.114$$

$$K_{3000K} = 0.114 \frac{\text{mol}}{\text{m}^3}$$

\rightarrow at 3000K the dissociation

$H_2 \rightleftharpoons 2H$ becomes appreciable

H/D exchange

$$m_H = 1.0078 \text{ g/mol} \quad m_D = 2.014 \text{ g/mol}$$

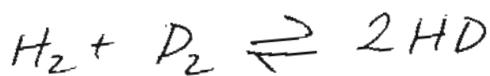
$\bar{\nu}_0$	H_2	HD	D_2
	4371 cm^{-1}	3786 cm^{-1}	3092 cm^{-1}

$$r_0 = 0.074 \text{ nm} \text{ for all molecules}$$

q_v and q_e are the same for all molecules
(assumption): K for H/D exchange

$$\Delta U_0 = N_A \Delta \varepsilon_0 \text{ zero-point energies}$$

$$\left. \begin{array}{l} H_2: \frac{1}{2} h c \bar{\nu}_0 = 4.341 \cdot 10^{-20} \text{ J} \\ HD: \frac{1}{2} h c \bar{\nu}_0 = 3.760 \cdot 10^{-20} \text{ J} \\ D_2: \frac{1}{2} h c \bar{\nu}_0 = 3.071 \cdot 10^{-20} \text{ J} \end{array} \right\} \varepsilon_0$$



$$\Delta \varepsilon_0 = \left[2 \varepsilon_0(HD) - \varepsilon_0(H_2) - \varepsilon_0(D_2) \right]$$

$$= 1.08 \cdot 10^{-21} \text{ J}$$

$$e^{-\Delta U_0/RT} = e^{-\frac{N_A \Delta \varepsilon_0}{RT}} = e^{-\frac{N_A \Delta \varepsilon_0}{N_A k_B T}}$$

$$= e^{-\frac{\Delta \varepsilon_0 / k_B T}{}} = 0.771$$

$$H_2: \mu = \frac{1}{2} m_H = \frac{m_H m_H}{m_H + m_H}$$

$$HD: \mu = \frac{m_H m_D}{m_H + m_D} \quad D_2: \mu = \frac{1}{2} m_D$$

$$\mu(k) \quad I(\text{kg m}^2) = \mu r_0^2$$

$$\underline{H_2 \quad 3.345 \cdot 10^{-27} \quad 4.583 \cdot 10^{-48}}$$

$$\underline{HD \quad 5.018 \cdot 10^{-27} \quad 6.109 \cdot 10^{-48}}$$

$$\underline{D_2 \quad 6.689 \cdot 10^{-27} \quad 9.157 \cdot 10^{-48}}$$

$$K = \frac{q^2(HD)}{q(H_2) q(D_2)} e^{-\Delta U_0 / RT} N^{-\sum_{\nu}}$$

$$\sum_{\nu} = 2 - 1 - 1 = 0$$

$$K = \frac{q^2(HD)}{q(H_2) q(D_2)} e^{-\Delta U_0 / RT}$$

$$\frac{q^2(HD)}{q(H_2) q(D_2)} = \frac{(2\pi \sigma_{HO} k_B T)^{3/2}}{h^6} \left(\frac{8\pi^2 I_{HO} k_B T}{\sigma_{HO} h^2} \right)^2 \cdot \frac{1}{q(H_2) q(D_2)}$$

q_v, q_e cancel (almost same in HD, H₂, D₂)

$$\sigma_{HO} = 1, \quad \sigma_{H_2} = \sigma_{D_2} = 2$$

$$\rightarrow K_c^o = \left(\frac{m_{HD}^2}{m_{H_2} m_{D_2}} \right)^{3/2} \cdot \frac{I_{HO}^2}{I_{H_2} I_{D_2}} \cdot \frac{\sigma_{H_2} \sigma_{D_2}}{\sigma_{HO}} e^{-\Delta U_0 / RT}$$

$$= 3.26 \rightarrow K_c = 3.26 \frac{\text{mol}}{\text{m}^3}$$