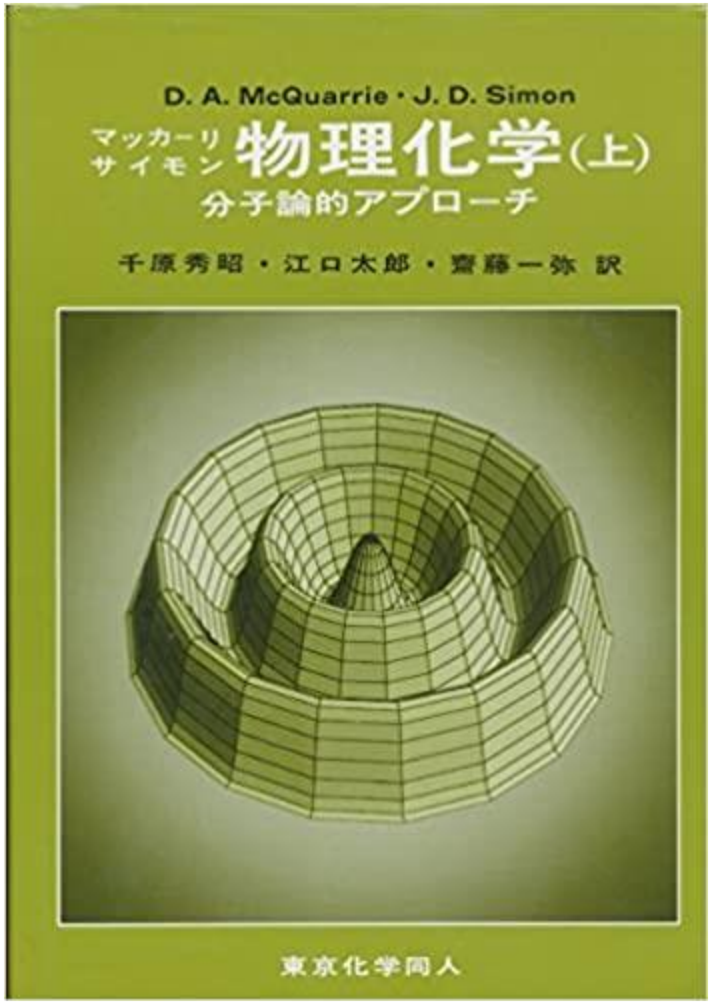
基礎機能化学　I

水曜3限（6/5～7/17）

担当：　北條　博彦



D. A. McQuarrie・J. D. Simon

マッカーリ
サイモン
物理化学（上）

分子論的アプローチ

千原秀昭・江口太郎・齋藤一弥 訳

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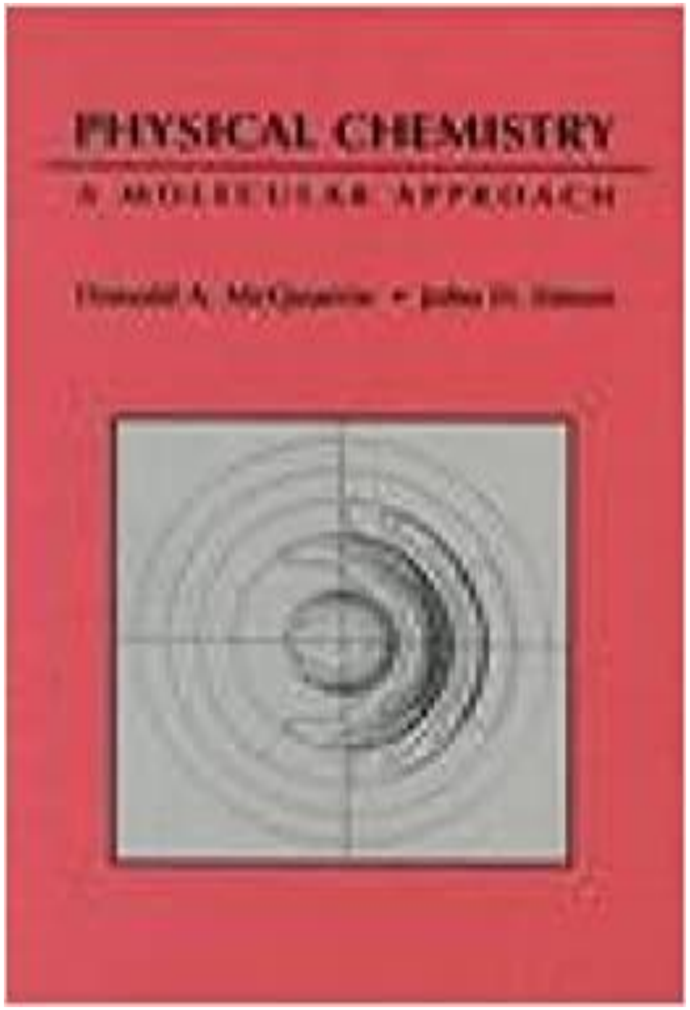
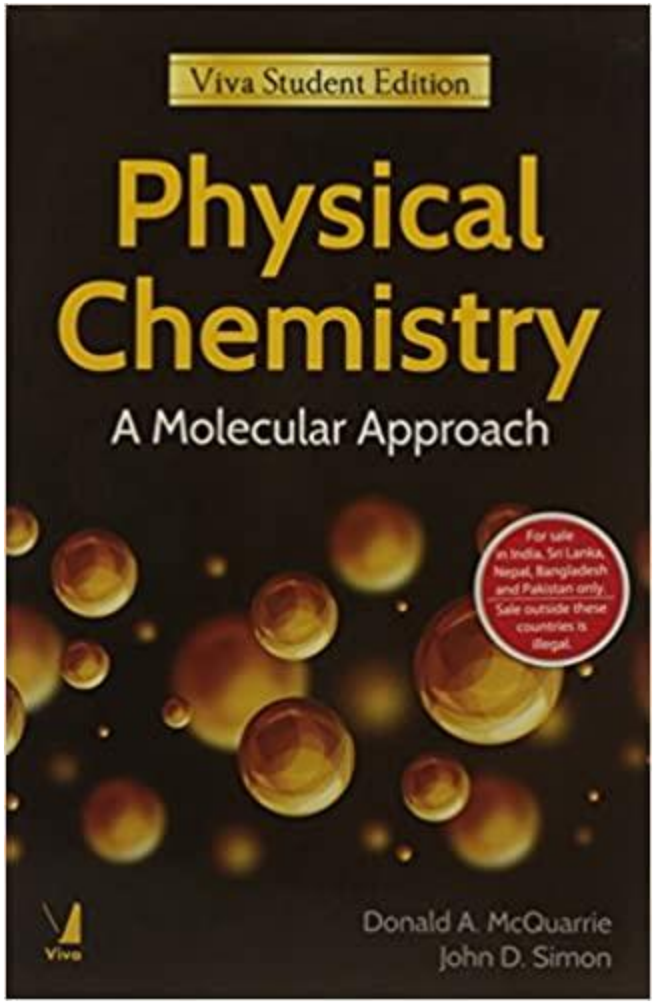


PHYSICAL CHEMISTRY

A MOLECULAR APPROACH

Donald A. McQuarrie • John D. Simon



Viva Student Edition

Physical Chemistry

A Molecular Approach

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Viva

Donald A. McQuarrie
John D. Simon

Chap. 1 The Dawn of the Quantum Theory

Chap. 5 The Harmonic Oscillator and the Rigid Rotor: Two spectroscopic Models

Chap. 13 Molecular Spectroscopy

Chap. 18 Partition Function and Ideal Gases

Chap. 20 Entropy and the Second Law of Thermodynamics

Chap. 26 Chemical Equilibrium

1. The Dawn of the Quantum Theory

How was science at the end of 19 century?

- Chemistry
  - periodic table of the elements and atomic weights
  - molecular structure of compounds
  - theory of chemical reactions

- Physics
  - generalization of Newtonian mechanics (= analytical mechanics)
  - thermodynamics and the concept of entropy
  - optics and electromagnetics

Physics of light: Maxwell's equations
Hertz's experiments of discharge
→ Light is electromagnetic wave.

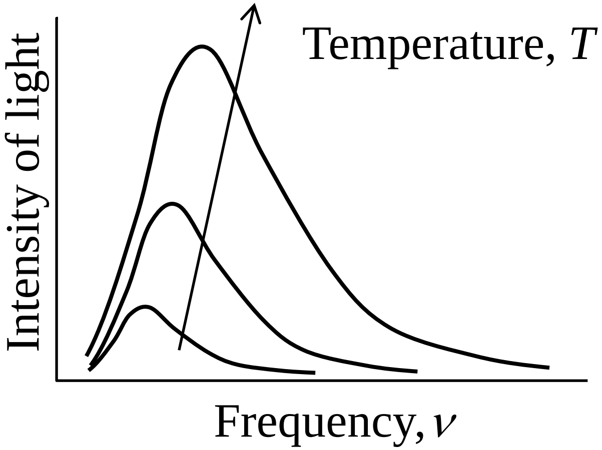
At the beginning of 20 century,

- The theory of relativity
- Quantum theory

→ Big switch of the existing physics

Quantum theory → Huge impact on chemistry, including
- atomic structure
- chemical bonding
- spectroscopy

1-1 Blackbody Radiation could not be Explained by Classical Mechanics.



Heated object emits light (= radiation).
Blackbody radiation law

$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi k_B T}{c^3}\nu^2\,d\nu$$

(Classical Rayleigh-Jeans law)
$\longrightarrow$ Ultraviolet catastrophe

1-2 Planck Used a Quantum Hypothesis to Derive the Blackbody Radiation Law.

Planck (1900) hypothesized that the electronic oscillation in a material is quantized ($E = h\nu$).

$$\Rightarrow\quad d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{k_B T}}-1}d\nu$$

Limit of $\dfrac{h\nu}{k_B T} << 1$ gives Rayleigh-Jeans formula.

Wien’s displacement law (empirical law): $\lambda_{\max}T = 2.90\times10^{-3}\ \mathrm{mK}$

Planck formula affords a coefficient 2.899×10^{-3} mK.

Blackbody radiation of 6000 K approximates the spectrum of sunlight.

1-3 Einstein Explained the Photoelectronic Effect with a Quantum Hypothesis.

Hertz (1887) found that metal surface emits electron when irradiated with light (= photoelectron effect).

→ Kinetic energy irrespective of the intensity of light
Threshold of frequency

Einstein (1905)

- explained photoelectronic effect using Planck formula.
- deduced that the emitted light is quantized (→photon).

$$KE = \frac{1}{2} m\upsilon^2 = h\nu - \phi$$

(ϕ is work function)

Table of work functions

Materials	ϕ / eV
Na	2.36
Au (100)	5.22
GaAs (100)	4.6
anthracene	4.71
Cu-phthalocyanine	4.56

1 eV = 1.602×10^{-19} J

1-4 The Hydrogen Atomic Spectrum Consists of Several Series of Lines.

Atoms at high temperature emits light (with specific frequency).

Balmer’s empirical formula (for Hydrogen’s emission spectrum line)

$$\nu = 8.2202 \times 10^{14} \times \left(1 - \frac{4}{n^2}\right) \text{ Hz}$$

excitations of n = 2 → n = 3, 4, 5・・・ (Balmer series)

1-5 The Rydberg Formula Accounts for All the Lines in the Hydrogen Atomic Spectrum.

Rydberg (~1887):

$$\tilde{\nu} = \frac{1}{\lambda} = 109680 \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1}$$

→ Rydberg constant (R_H)

Similar formula can hold for other atomic spectrum line

$$\tilde{\nu} \propto \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1} \Rightarrow \text{ Ritz's combination rule}$$

1-6 Louis de Broglie Postulated that Matter has Wavelike Properties

$$\left.\begin{array}{r}\text{Physical description of light: wave-like}\\ \text{particle-like}\end{array}\right\} \longrightarrow \text{wave-particle duality}$$

Einstein (theory of relativity)

$$\lambda = \frac{h}{p} \qquad \left(p = \frac{h}{\lambda} = \frac{k}{2\pi} h = k\hbar \right)$$

de Broglie formula

$$\lambda = \frac{h}{m\upsilon} \quad \text{(de Broglie wavelenghth)}$$

Moving particle	λ / pm
100 V electron	120
Ra α ray	6.6×10^{-3}
golf ball	4.9×10^{-22}

1-7 de Broglie Waves are Observed Experimentally

X ray beam → X ray diffraction
electron beam → electron (beam) diffraction → TEM

Physical description of electron:
particle-like (J.J. Thomson, Nobel prize winner (1906))
wave-like (G.P. Thomson, Nobel prize winner (1937))

1-8 The Bohr Theory of the Hydrogen Atom can be Used to Derive the Rydberg Formula

Bohr's hydrogen atom model

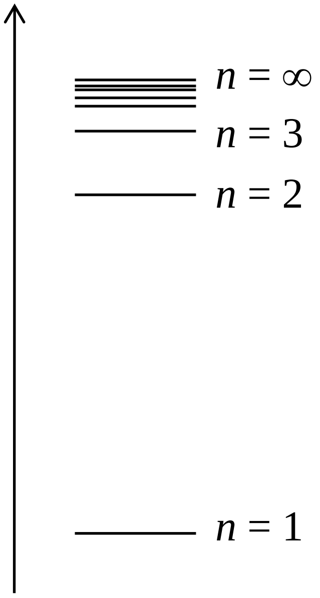
Balance of Coulombic force and centrifugal force

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m\upsilon^2}{r} \quad \Rightarrow \quad \text{classically forbidden (unsustainable motion)}$$

Introduction of non-classic condition

$$2\pi r = n\lambda \qquad (\lambda\text{: de Broglie wavelength})$$

$$m\upsilon r = n\hbar \qquad \text{(quantization of angular momentum)}$$



$$r = \frac{4\pi\varepsilon_0 \hbar^2 n^2}{me^2} = 5.292\times 10^{-11}\ \text{m} \quad (\text{Bohr radius } (a_0))$$

$$E = -\frac{e^2}{8\pi\varepsilon_0 r} = -\frac{me^4}{8\pi\varepsilon_0^2 h^2}\frac{1}{n^2}$$

$$\Delta E = \frac{me^4}{8\pi\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu \qquad \text{(Bohr frequency condition)}$$

$\longrightarrow$ 109737 cm^{-1} $\equiv R_\infty$ (*cf.* R_H = 109680 cm^{-1})

($2R_\infty$ is used as atomic unit of energy)

1-9 The Heisenberg Uncertainty Principle States the Position and the Momentum of a Particle Cannot be Specified Simultaneously with Unlimited Precision

Resolution of microscope $\Delta x \cong \lambda$ (wavelength of light)

Momentum of light $p = \dfrac{h}{\lambda}$ ⇒ partially transferred to electrons

$\Delta x \cdot \Delta p \geq h$ Uncertainty principle

↓

Conflict with Bohr theory

↓

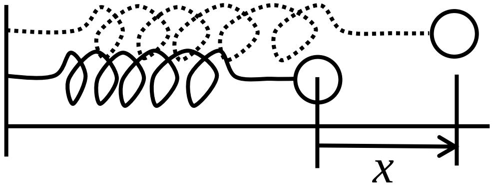
Construction of new quantum theory

5. The Harmonic Oscillator and the Rigid Rotor: Two spectroscopic Models

$$\begin{cases} \text{Harmonic Oscillator} \longrightarrow \text{Vibrational spectra (Force constants of molecules)} \\ \text{Rigid Rotor} \longrightarrow \text{Rotational spectra (Bond lengths)} \end{cases}$$

$$\text{Classical} \begin{cases} \text{oscillator} \\ \text{rotor} \end{cases} \Rightarrow \text{quantum mechanical representation of energy}$$

5-1 A Harmonic Oscillator Obeys Hook's Law.



$$f = -kx$$

k: force constant

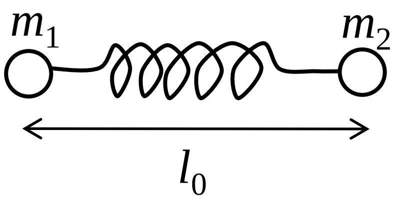
$$x(t) = C_1 \sin \omega t + C_2 \sin \omega t$$
$$= C \exp\left[i(\omega t - \varphi)\right]$$
$$\omega = \sqrt{\frac{k}{m}}$$

$$V(x) = -\int f(x)\,\mathrm{d}x$$
$$= \frac{k}{2} x^2 + V(0)$$

$$K = \frac{kA^2}{2} \sin^2 \omega t,\ V = \frac{kA^2}{2} \cos^2 \omega t,\ \ E = K + V = \frac{kA^2}{2}$$

5-2 The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule.

Two particles connected with a spring



$$\begin{cases} m_1 \dfrac{\mathrm{d}x_1}{\mathrm{d}t^2} = k(x_2 - x_1 - l_0) \\ m_2 \dfrac{\mathrm{d}x_1}{\mathrm{d}t^2} = -k(x_2 - x_1 - l_0) \end{cases}$$

centroid coordinate

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$(m_1 + m_2)\frac{\mathrm{d}^2 X}{\mathrm{d}t^2} = 0$$

relative coordinate

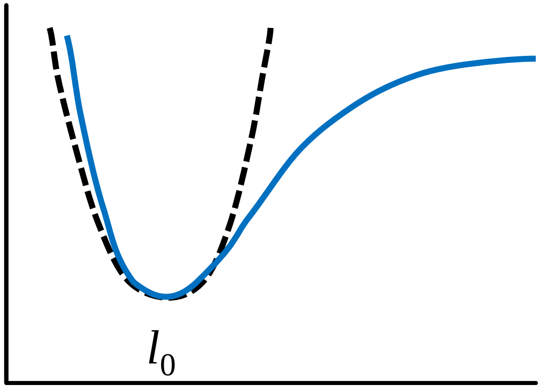
$$x = x_2 - x_1 - l_0$$

$$\frac{m_1 m_2}{m_1 + m_2}\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + kx = 0$$

$$x = C\exp[i(\omega t - \phi)]$$

$$\omega = \sqrt{\frac{k}{\mu}} \qquad \left(\mu = \frac{m_1 m_2}{m_1 + m_2}\right)$$

5-3 The Harmonic Oscillator Approximation Results from the Expansion of an Internuclear Potential Around its Minimum.



Taylor expansion

$$V(l) = V(l0) + \frac{\mathrm{d}V}{\mathrm{d}l^2}(l - l_0) + \frac{1}{2!}\frac{\mathrm{d}^2 V}{\mathrm{d}l^2}(l - l_0)^2 + \cdots$$

$$V(x) = \frac{1}{2}kx^2 + \underline{\frac{1}{6}\gamma x^3 + \cdots}$$

anharmonic terms
(→ Chapter 13)

5-4 The Energy levels of a Quantum-Mechanical Harmonic Oscillator is $\mathbf{E_v = \hbar\omega\left(v+\frac{1}{2}\right)}$, where v = 0, 1, 2, …

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi(x)=E\psi(x), \quad V(x)=\frac{1}{2}kx^2$$

$$E_v=\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right)$$

$$=\hbar\omega\left(v+\frac{1}{2}\right)$$

$$E_0=\hbar\omega\left(0+\frac{1}{2}\right)=\frac{1}{2}\hbar\omega$$

zero-point energy

5-5 The Harmonic Oscillator Accounts for the Infrared Spectrum of a Diatomic Molecule.

$$E_v=\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right) \qquad v=0,1,2,\cdots$$

$$\Delta E=h\nu_{\text{obs}} \quad \Delta v=\pm 1$$

$$=E_{v+1}-E_v=\hbar\sqrt{\frac{k}{\mu}}$$

$$\nu_{\text{obs}}=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \left(\tilde{\nu}_{\text{obs}}=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\right)$$

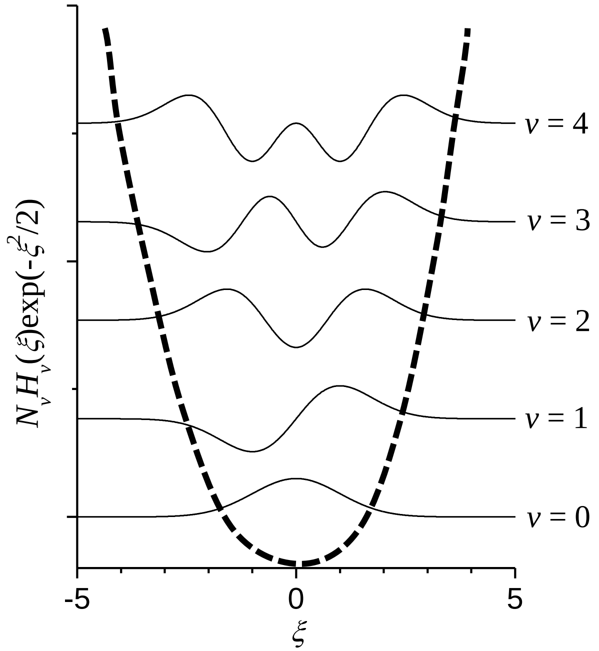
Compound	k / N m^{-1}	$\tilde{\nu}$ / cm^{-1}
H_2	510	4401
D_2	527	2990
$H^{35}Cl$	478	2886
$^{16}O_2$	1142	1556
$^{14}N_2$	2243	2330
$^{12}C^{16}O$	1857	2143

5-6 The Harmonic-Oscillator Wave Functions Involve Hermite Polynomials.

$$\psi_v(x) = N_v H_v(\sqrt{\alpha}\,x)\exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}, \quad N_v = \frac{1}{\sqrt{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\left.\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi \\ &\vdots \end{aligned}\right\} \quad \frac{\mathrm{d}H_v(\xi)}{\mathrm{d}\xi} = 2vH_{v-1}(\xi)$$



$$\int \psi_v{}^*(x)\,\psi_{v'}(x)\,\mathrm{d}x = \delta_{vv'} \quad \text{orthonormalized}$$

5-7 Hermite Polynomials are Either Even or Odd Functions.

$$\psi_v(-x) = \begin{cases} \psi_v(x) & (v:\text{even}) \\ -\psi_v(x) & (v:\text{odd}) \end{cases}$$

Average of the position

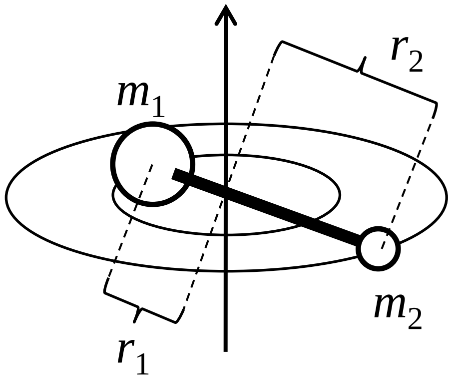
$$\langle x \rangle = \int \psi_v{}^*(x)\,x\,\psi_v(x)\,\mathrm{d}x = 0$$

Average of the momentum

$$\langle p \rangle = \int \psi_v{}^*(x)\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_v(x)\,\mathrm{d}x = 0$$

5-8 The Energy Levels of a Rigid Rotor is $\mathbf{E} = \hbar^2 \mathbf{J}(\mathbf{J}+1)/2\mathbf{I}$.

Rigid-rotor model: bond length holds unchanged during rotation.



$$v_1 = 2\pi r_1 \nu_{\text{rot}} = r_1\omega,\ v_2 = 2\pi r_2 \nu_{\text{rot}} = r_2\omega$$

$$K = \frac{1}{2}m_1{v_1}^2 + \frac{1}{2}m_2{v_2}^2 = \frac{1}{2}I\omega^2$$

$$I = m_1{r_1}^2 + m_2{r_2}^2 = \frac{m_1 m_2}{m_1+m_2}(r_1+r_2)^2 \equiv \mu r^2$$

Angular momentum $L = I\omega$

Kinetic Energy $K = \dfrac{L^2}{2I}$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\frac{\partial^2}{\partial r^2}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right\}$$

$$= -\frac{\hbar^2}{2\mu}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\frac{\partial^2}{\partial r^2}\right)\right\} + \frac{\hat{L}^2}{2I}$$

$\hat{L}^2 Y(\theta,\varphi) = \hbar^2 J(J+1)Y(\theta,\varphi)$ $\qquad$ $Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$: spherical harmonics

5-8 The Energy Levels of a Rigid Rotor is $E = \hbar^2 J(J+1)/2I$. (cont.)

l	m	$\Theta_{l,m}(\theta)$	$\Phi_m(\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
1	0	$\frac{\sqrt{3}}{\sqrt{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
1	± 1	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i\varphi)$
2	0	$\frac{\sqrt{5}}{2\sqrt{2}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$
2	± 1	$\frac{\sqrt{30}}{2\sqrt{2}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i\varphi)$
2	± 2	$\frac{\sqrt{30}}{4\sqrt{2}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i2\varphi)$
3	0	$\frac{\sqrt{7}}{2\sqrt{2}}(5\cos^3\theta - 3\cos\theta)$	$\frac{1}{\sqrt{2\pi}}$
3	± 1	$\frac{\sqrt{21}}{4\sqrt{2}}\sin\theta(5\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i\varphi)$
3	± 2	$\frac{\sqrt{210}}{4\sqrt{2}}\sin^2\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i2\varphi)$
3	± 3	$\frac{\sqrt{35}}{4\sqrt{2}}\sin^3\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i3\varphi)$

5-9 The Rigid Rotor is a Model for a Rotating Diatomic Molecule.

Selection rule among rotation levels: $\Delta J = \pm 1$

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I}\{(J+1)(J+2) - J(J+1)\}$$

$$= \frac{\hbar^2}{I}(J+1), \qquad J = 0, 1, 2, \cdots$$

I of diatomic molecule is 10^{-45}~10^{-46} kg m^2

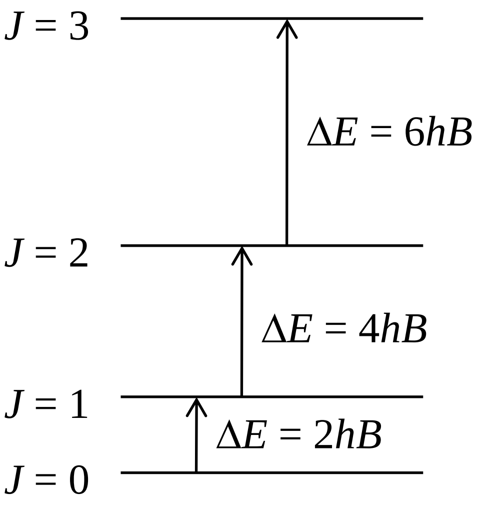
⇒ $\nu = 10^{10}$~10^{11} Hz (microwave region)

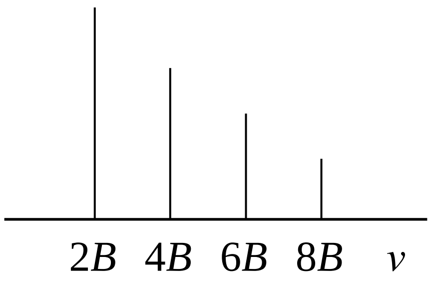
$$\nu = 2B(J+1), \ \ J = 0, 1, 2, \cdots$$

$$B = \frac{h}{8\pi^2 I}, \ \ \tilde{B} = \frac{h}{8\pi^2 cI}$$

B: rotational constant

Microwave absorption spectra show serial peaks at $2B$ intervals.





13. Molecular Spectroscopy

Microwave absorption spectroscopy
Infrared absorption spectroscopy

Classical models → normal-mode analysis, selection rule, group theory, etc.

13-1 Different Regions of the Electromagnetic Spectrum are Used to Investigate Different Molecular Processes

Region	Microwave	Far IR	Infrared	Vis-UV
ν / Hz	$10^{9} \sim 10^{11}$	$10^{11} \sim 10^{13}$	$10^{13} \sim 10^{14}$	$10^{14} \sim 10^{16}$
λ / m	$0.3 \sim 3\mathrm{x}10^{-3}$	$3\mathrm{x}10^{-3} \sim 10^{-5}$	$3\mathrm{x}10^{-5} \sim 7\mathrm{x}10^{-7}$	$7\mathrm{x}10^{-5} \sim 2\mathrm{x}10^{-7}$
$\tilde{\nu}$ / cm^{-1}	$0.033 \sim 3.3$	$3.3 \sim 330$	$330 \sim 14500$	$14500 \sim 50000$
E / J molecule^{-1}	$6.6\mathrm{x}10^{-25} \sim 6.6\mathrm{x}10^{-23}$	$6.6\mathrm{x}10^{-23} \sim 6.6\mathrm{x}10^{-21}$	$6.6\mathrm{x}10^{-21} \sim 2.9\mathrm{x}10^{-19}$	$2.9\mathrm{x}10^{-19} \sim 1.0\mathrm{x}10^{-18}$
process	rotation of polynuclear molecule	rotation of small molecule	vibration of flexible molecule	electronic transition

13-2 Rotational Transitions Accompany Vibrational Transitions.

Harmonic oscillator

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)h\nu \quad \upsilon = 0, 1, 2, \cdots$$

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

Energy of molecular vibration

$$G(\upsilon) = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu} \quad (= E/hc)$$

Rigid rotor

$$E_J = \frac{\hbar^2}{2I}J(J+1) \quad J = 0, 1, 2, \cdots$$

degeneracy $g_J = 2J + 1$

Energy of molecular rotation

$$F(J) = \tilde{B}J(J+1) \quad (= E_J/hc)$$

$$E_{\upsilon,J} = G(\upsilon) + F(J) = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu} + \tilde{B}J(J+1)$$

ca. 100 ~ 1000 : 1

13-2 Rotational Transitions Accompany Vibrational Transitions. (cont.)

$$\text{Selection rule} \begin{cases} \Delta\upsilon = +1 \\ \Delta J = \pm 1 \end{cases}$$

when $\Delta J = +1$

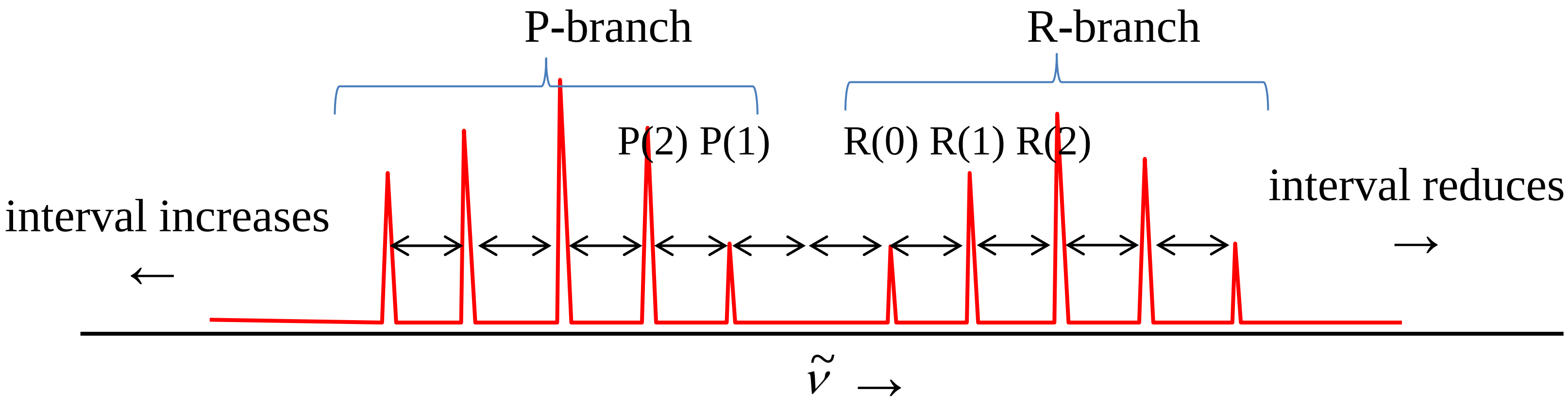
$$\tilde{\nu}_{\text{obs}} = \tilde{E}_{\upsilon+1,\,J+1} - \tilde{E}_{\upsilon,\,J}$$

$$= \tilde{\nu} + 2\tilde{B}(J+1) \quad J = 0, 1, 2, \cdots \quad \text{(R-branch)}$$

when $\Delta J = -1$

$$\tilde{\nu}_{\text{obs}} = \tilde{E}_{\upsilon+1,\,J-1} - \tilde{E}_{\upsilon,\,J}$$

$$= \tilde{\nu} - 2\tilde{B}J \quad J = 1, 2, \cdots \quad \text{(P-branch)}$$



13-3 Vibration-Rotation Interaction Accounts for the Unequal Spacing of the Lines in the P and R Branches of a Vibration-Rotation Spectrum

$$E_{\upsilon,J} = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu} + \tilde{B}J(J+1)$$

$$\tilde{B} = \frac{h}{8\pi c\mu R_\mathrm{e}^{\;2}}$$

R_e increases with increasing υ

$\Rightarrow B$ decreases ($B_1 < B_0$)

when $\upsilon = 0 \rightarrow 1$

$$\tilde{\nu}_\mathrm{R}(\Delta J = +1) = \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

$$\tilde{\nu}_\mathrm{P}(\Delta J = -1) = \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J-1)J - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} - (\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

$$\tilde{B}_\upsilon = \tilde{B}_\mathrm{e} - \tilde{\alpha}_\mathrm{e}\left(\upsilon + \frac{1}{2}\right)$$

For $^{1}\mathrm{H}^{127}\mathrm{I}$: $\tilde{B}_\mathrm{e} = 6.508\,\mathrm{cm}^{-1}$, $\tilde{\alpha}_\mathrm{e} = 0.168\,\mathrm{cm}^{-1}$

13-4 The Lines in a Pure Rotational Spectrum are not Equally Spaced

Molecule rotates vigorously ⇒ bonds are lengthened (→ I increases)

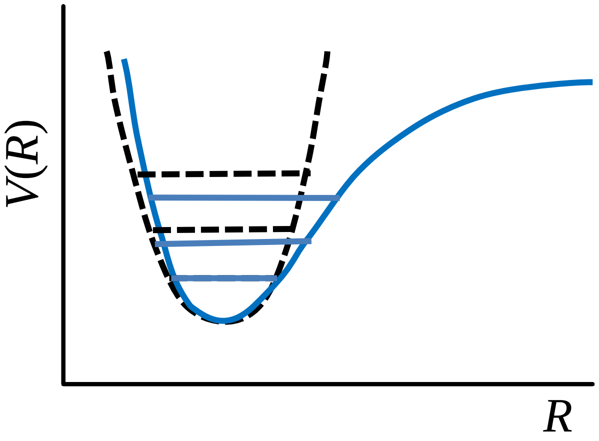
$$F(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

$\tilde{D}$: centrifugal distortion constant

$$\begin{aligned}\tilde{\nu} &= F(J+1) - F(J) \\ &= 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3\end{aligned}$$

For $^{1}\mathrm{H}^{35}\mathrm{Cl}$: $\tilde{B} = 10.403\,\mathrm{cm}^{-1}$ $\tilde{D} = 0.00044\,\mathrm{cm}^{-1}$

13-5 Overtones are Observed in Vibrational Spectra



$$V(R) = V(R_e) + \frac{1}{2!}\frac{d^2V}{dR^2}(R - R_e)^2 + \cdots$$

$$= \frac{k}{2}x^2 + \frac{\gamma_3}{6}x^3 + \frac{\gamma_4}{24}x^4 \cdots$$

$$G(\upsilon) = \tilde{\nu}_e\left(\upsilon + \frac{1}{2}\right) - \tilde{x}_e\tilde{\nu}_e\left(\upsilon + \frac{1}{2}\right)^2 + \cdots$$

$\tilde{x}_e (<<1)$: anharmonicity constant

selection rule : $\Delta\upsilon = \pm 1, \pm 2, \pm 3, \cdots$ intensity is weakened over 2nd harmonic.

$$\tilde{\nu}_{obs} = G(\upsilon) - G(0) = \tilde{\nu}_e\upsilon - \tilde{x}_e\tilde{\nu}_e\upsilon(\upsilon + 1)$$

For $^1H^{35}Cl$: $\tilde{\nu}_e = 2990.9\,\mathrm{cm}^{-1}$, $\tilde{x}_e\tilde{\nu}_e = 52.82\,\mathrm{cm}^{-1}$

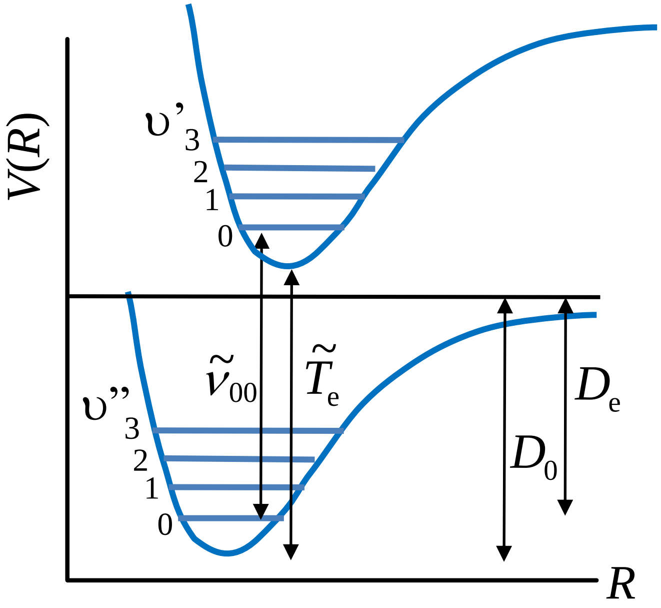
13-6 Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

Energy gap between electronic levels → visible ~ ultraviolet

Each level is accompanied by vibrational and rotational levels.

Born-Oppenheimer approximation: Electronic and rovibrational levels are independent.

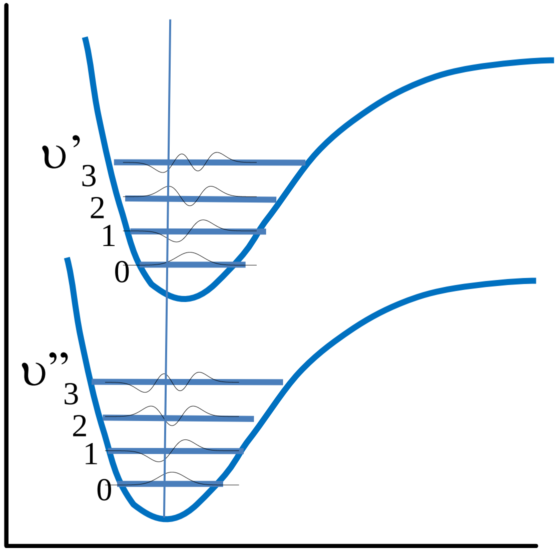
$$
\begin{aligned}
E_{\text{total}} &= \tilde{\nu}_{\text{el}} + G(\upsilon) + F(J) \\
&= \tilde{\nu}_{\text{el}} + \left(\upsilon + \frac{1}{2}\right)\tilde{\nu} - \tilde{x}_{\text{e}}\tilde{\nu}_{\text{e}}\left(\upsilon + \frac{1}{2}\right)^2 + \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2
\end{aligned}
$$

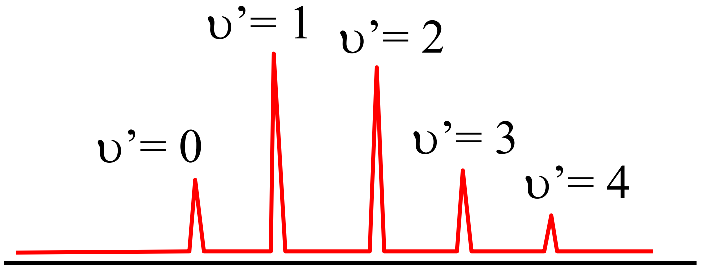


$$
\begin{aligned}
\tilde{\nu}_{\text{obs}} &= \tilde{T}_{\text{e}} + \left(\frac{1}{2}\tilde{\nu}'_{\text{e}} - \frac{1}{4}\tilde{x}'_{\text{e}}\tilde{\nu}'_{\text{e}}\right) - \left(\frac{1}{2}\nu''_{\text{e}} - \frac{1}{4}\tilde{x}''_{\text{e}}\nu''_{\text{e}}\right) \\
&\quad + \tilde{\nu}'_{\text{e}}\upsilon' - \tilde{x}'_{\text{e}}\tilde{\nu}'\upsilon'(\upsilon'+1)
\end{aligned}
$$

$$
= \tilde{\nu}_{00} + \tilde{\nu}_{\text{e}}\upsilon' - \tilde{x}'_{\text{e}}\tilde{\nu}'\upsilon'(\upsilon'+1) \qquad \upsilon' = 0, 1, 2, \cdots
$$

13-7 The Franck-Condon Principle Predicts the Relative Intensities of Vibronic Transitions





Internuclear distance is almost unchanged.
⇒ Frank-Condon principle

13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule

Moment of inertia	I_{xx}, I_{yy}, I_{zz} (moment of inertia around axes)
Product of inertia	$I_{xy}, I_{yz}, I_{zx}, I_{yx}, I_{zy}, I_{xz}$

$$\begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \to \begin{pmatrix} I_{\mathrm{A}} & 0 & 0 \\ 0 & I_{\mathrm{B}} & 0 \\ 0 & 0 & I_{\mathrm{C}} \end{pmatrix}$$

Diagonalization is realized for a certain coordinate system.
⇒ principal moment of inertia ($I_{\mathrm{A}} \le I_{\mathrm{B}} \le I_{\mathrm{C}}$)

13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule. (cont.)

Rotational constants: $\tilde{A} \geq \tilde{B} \geq \tilde{C}$

$$\tilde{A} = \frac{h}{8\pi^2 c I_\mathrm{A}}, \ \tilde{B} = \frac{h}{8\pi^2 c I_\mathrm{B}}, \ \tilde{C} = \frac{h}{8\pi^2 c I_\mathrm{C}}$$

○spherical top

$I_\mathrm{A} = I_\mathrm{B} = I_\mathrm{C}$

○symmetrical top

$I_\mathrm{A} < I_\mathrm{B} = I_\mathrm{C}$ (prolate)

$I_\mathrm{A} = I_\mathrm{B} < I_\mathrm{C}$ (flat)

○asymmetrical top

$I_\mathrm{A} \neq I_\mathrm{B} \neq I_\mathrm{C}$

Energy levels of prolate symmetric top

$$F(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$

Energy levels of flat symmetrical top

$$F(J,K) = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$$

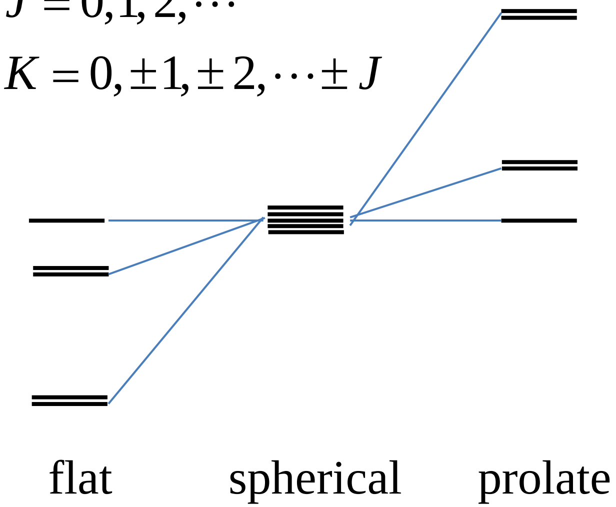
selection rules: $\Delta J = 0, \pm 1 \ \ \Delta K = 0 \ \ (K \neq 0)$

$\Delta J = \pm 1 \ \ \Delta K = 0 \ \ (K = 0)$

Polynuclear molecules have small stiffness.
⇒ large centrifugal distortion

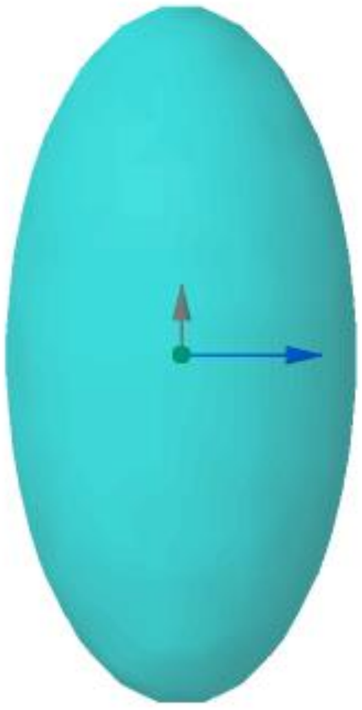
$J = 0, 1, 2, \cdots$

$K = 0, \pm 1, \pm 2, \cdots \pm J$



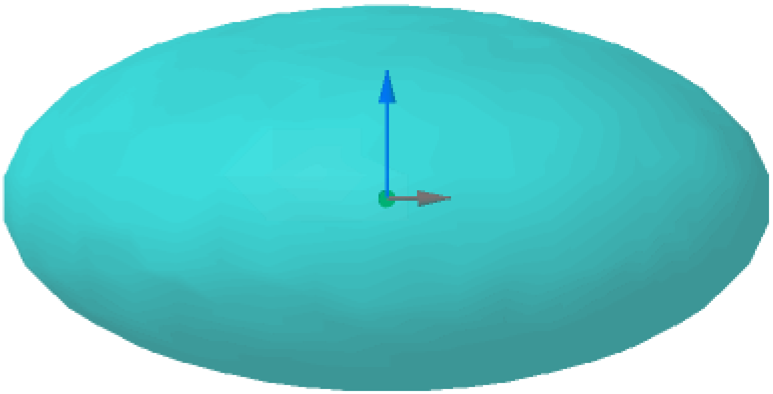
13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule. (cont.)

Prolate symmetrical top



13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule. (cont.)

Flat symmetrical top



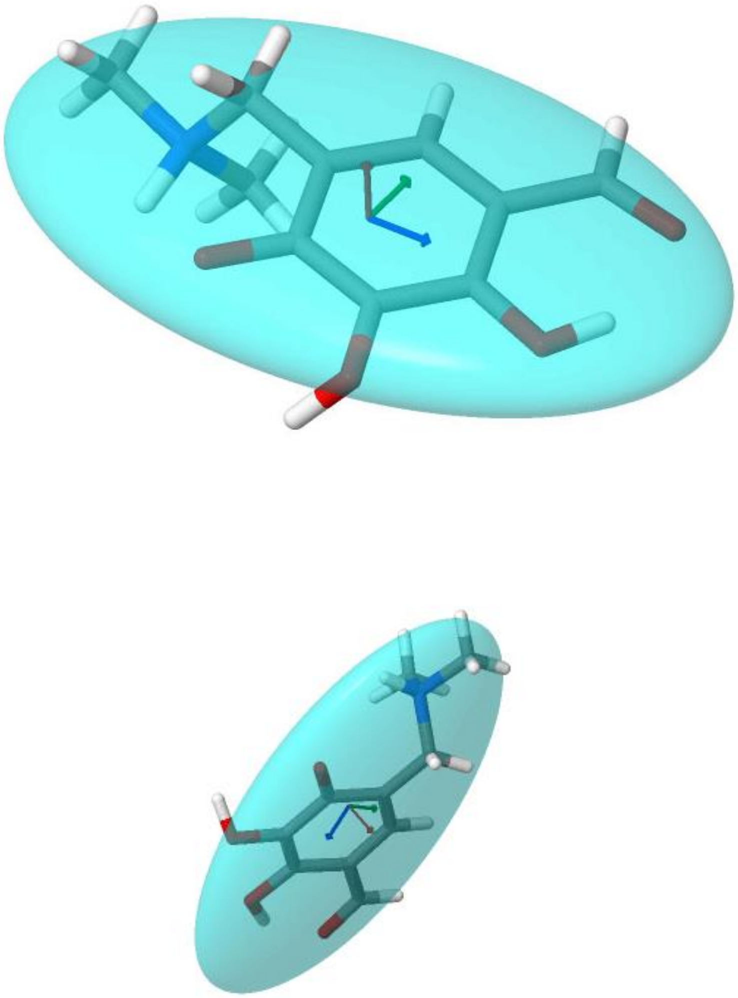
Center of Mass
4.570 3.016 5.231

Molecular Weight
211.084

Tensor of Inertia
1674.674 45.952 106.506
45.952 1179.412 338.680
106.506 338.680 678.149

Principal Moment of Inertia
1701.819 1327.732 502.684

Principal Axes
0.968 0.191 0.164
0.244 -0.876 -0.417
-0.064 -0.443 0.894



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13-9 The Vibrations of Polyatomic Molecules are Represented by Normal Coordinates.

$$\begin{array}{l}\text{A molecule consisting}\\ \text{of } N \text{ atoms has}\end{array} \rightarrow \begin{array}{c}3N \text{ degree}\\ \text{of freedom}\end{array} \begin{cases} 3 \text{ translational} \\ 3 \text{ rotational (2 for linear molecule)} \\ 3N\text{-6 vibrational (}3N\text{-5 for linear molecule)} \end{cases}$$

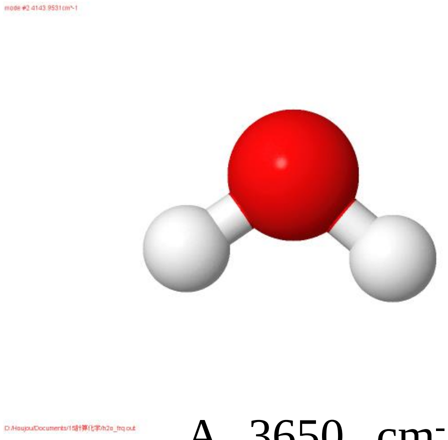
$$V(q_1,q_2,\cdots q_{3N-6}) = V(0,0,\cdots 0) + \underbrace{\frac{1}{2}\sum_i\sum_j\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)q_i q_j} + \cdots$$

$$\Rightarrow \frac{1}{2}\sum_i\sum_j f_{ij} q_i q_j$$

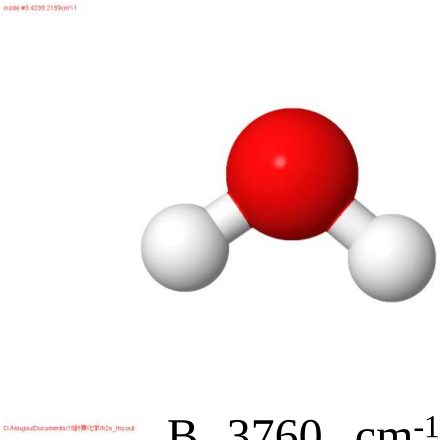
$$= \frac{1}{2}\sum_j F_j Q_j^{\ 2} \qquad \left\{Q_j\right\} \ \text{normal mode coordinate}$$

$$\left.\begin{aligned} \hat{H}_{\text{vib}} &= -\sum_j \frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}Q^2} + \frac{1}{2}\sum_j F_j Q_j^{\ 2} \\ &= \sum_j\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}Q^2} + \frac{1}{2}F_j Q_j^{\ 2}\right) \equiv \sum_j \hat{H}_{\text{vib},j} \\ \psi_{\text{vib}}(Q_1,Q_2,\cdots Q_{3N-6}) &= \psi_{\text{vib},1}(Q_1)\psi_{\text{vib},2}(Q_2)\cdots\psi_{\text{vib},3N\text{-}6}(Q_{3N-6}) \end{aligned}\right\} \Rightarrow E = \sum_j h\nu_j\left(\upsilon_j + \frac{1}{2}\right)$$

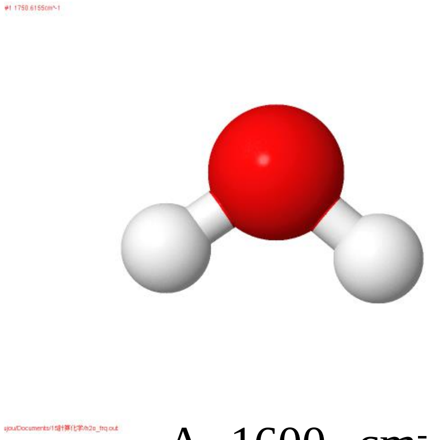
Normal modes of H_2O



A_1 3650 cm^{-1}



B_2 3760 cm^{-1}

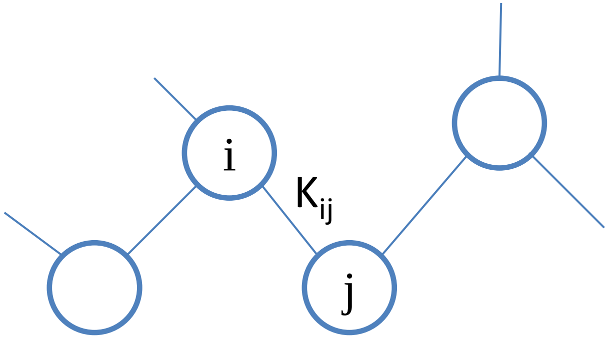


A_1 1600 cm^{-1}

Selection rule: $$\left.\begin{array}{l}\Delta\upsilon = +1 \\ \Delta J = \pm 1\end{array}\right\}$$ Dipole moment is parallel to bond axis.

$$\left.\begin{array}{l}\Delta\upsilon = +1 \\ \Delta J = 0, \pm 1\end{array}\right\}$$ Dipole moment is perpendicular to bond axis.

Equation of motion for coupled oscillator



$$F_{ix} = m_i \frac{d^2}{dt^2} x_i$$

$$= \sum_j \frac{d^2\phi}{dx_i dx_j}(x_j - x_i) \equiv \sum_j k_{ij}(x_j - x_i)$$

$$\left.\begin{array}{l} K_{ij} = -k_{ij} \\ K_{ii} = \sum_j k_{ij} \end{array}\right\} \Rightarrow F_{ix} = -\sum_j K_{ij} x_j$$

$$x_i = x_{0i} \exp(-i\omega t)$$

$$\Rightarrow F_{ix} = -m_i \omega^2 x_i$$

$$\sum_j K_{ij} x_j = m_i \omega^2 x_i \Rightarrow Kx = Mx\omega^2$$

$$V = \frac{1}{2} x^t K x = \frac{1}{2} x^t M x \omega^2$$

φ: two-body potential
When a force proportional to displacement is taken into account, it is called harmonic approximation.

K: stiffness matrix

Oscillating *x* is assumed as a solution.

Simultaneous equations for all the particles.
→ An equation of matrix

V: Vibrational energy

Hessian method

$$M^{-1}Kx = x\omega^2$$

$$M = \begin{pmatrix} m_1 & & & & & & \\ & m_1 & & & & 0 & \\ & & m_1 & & & & \\ & & & \ddots & & & \\ & & & & m_N & & \\ & 0 & & & & m_N & \\ & & & & & & m_N \end{pmatrix}, \quad K = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & & & & \\ \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial y_1^2} & \frac{\partial^2 U}{\partial y_1 \partial z_1} & \cdots & & \cdots & \\ \frac{\partial^2 U}{\partial z_1 \partial x_1} & \frac{\partial^2 U}{\partial z_1 \partial y_1} & \frac{\partial^2 U}{\partial z_1^2} & & & & \\ & \vdots & & \ddots & & & \\ & & & & \frac{\partial^2 U}{\partial x_N^2} & \frac{\partial^2 U}{\partial x_N \partial y_N} & \frac{\partial^2 U}{\partial x_N \partial z_N} \\ & \vdots & & & \frac{\partial^2 U}{\partial y_N \partial x_N} & \frac{\partial^2 U}{\partial y_N^2} & \frac{\partial^2 U}{\partial y_N \partial z_N} \\ & & & & \frac{\partial^2 U}{\partial z_N \partial x_N} & \frac{\partial^2 U}{\partial z_N \partial y_N} & \frac{\partial^2 U}{\partial z_N^2} \end{pmatrix}$$

$$M^{-1} = \begin{pmatrix} \mu_1 & & & & & & \\ & \mu_1 & & & & 0 & \\ & & \mu_1 & & & & \\ & & & \ddots & & & \\ & & & & \mu_N & & \\ & 0 & & & & \mu_N & \\ & & & & & & \mu_N \end{pmatrix}, \quad x = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_N \\ y_N \\ z_N \end{pmatrix}$$

x is an eigenvector of $M^{-1}K$.
→ You have to find a set of x that diagonalizes $M^{-1}K$.

Mass-weighted Hessian method

$$M^{-1}Kx = x\omega^2$$

M^{-1}K is not a symmetric matrix.
→x's are not orthogonal to each other.
→ω is not necessarily real.

$$M^{-1/2}KM^{-1/2}M^{1/2}x = M^{1/2}x\omega^2$$

$$M^{1/2} = \begin{pmatrix} \sqrt{m_1} & & & & & & \\ & \sqrt{m_1} & & & & 0 & \\ & & \sqrt{m_1} & & & & \\ & & & \ddots & & & \\ & & & & \sqrt{m_N} & & \\ & 0 & & & & \sqrt{m_N} & \\ & & & & & & \sqrt{m_N} \end{pmatrix}$$

When we multiply M$^{1/2}$ on the both hands of the equation.

M is a diagonal matrix.
→$M^{1/2}$ is easily obtained.

$$\left.\begin{aligned} M^{-1/2}KM^{-1/2} &\equiv D \\ M^{1/2}x &\equiv w \end{aligned}\right\} \Rightarrow Dw = w\omega^2 \qquad D_{ij} = \sqrt{\mu_i}\sqrt{\mu_j}K_{ij}$$

D is symmetrical matrix.
→so-called dynamical matrix

Natural oscillation of a diatomic molecule (cont.)

mass-weighted coordinate (orthonormalized)

$$\hat{\mathbf{W}} = \frac{1}{\sqrt{\mu_1 + \mu_2}} \begin{pmatrix} \sqrt{\mu_2} & \sqrt{\mu_1} \\ \sqrt{\mu_1} & -\sqrt{\mu_2} \end{pmatrix}$$

Cartesian coordinate

$$\mathbf{X} = \mathbf{M}^{-1/2}\hat{\mathbf{W}} = \frac{1}{\sqrt{\mu_1 + \mu_2}} \begin{pmatrix} \sqrt{\mu_1\mu_2} & \mu_1 \\ \sqrt{\mu_1\mu_2} & -\mu_2 \end{pmatrix}$$

Cartesian coordinate (normalized)

$$\hat{\mathbf{X}} = \frac{1}{\sqrt{2(\mu_1^2 + \mu_2^2)}} \begin{pmatrix} \sqrt{\mu_1^2 + \mu_2^2} & \sqrt{2}\mu_1 \\ \sqrt{\mu_1^2 + \mu_2^2} & -\sqrt{2}\mu_2 \end{pmatrix}$$

modal mass matrix

$$\hat{\mathbf{X}}^{\mathrm{T}}\mathbf{M}\hat{\mathbf{X}} = \begin{pmatrix} \dfrac{\mu_1 + \mu_2}{2\mu_1\mu_2} & 0 \\ 0 & \dfrac{\mu_1 + \mu_2}{\mu_1^2 + \mu_2^2} \end{pmatrix} \equiv \begin{pmatrix} m_{\mathrm{T}} & 0 \\ 0 & m_{\mathrm{V}} \end{pmatrix}$$

modal stiffness matrix

$$\hat{\mathbf{X}}^{\mathrm{T}}\mathbf{K}\hat{\mathbf{X}} = \begin{pmatrix} 0 & 0 \\ 0 & \dfrac{(\mu_1 + \mu_2)^2}{\mu_1^2 + \mu_2^2} K \end{pmatrix} \equiv \begin{pmatrix} K_{\mathrm{T}} & 0 \\ 0 & K_{\mathrm{V}} \end{pmatrix}$$

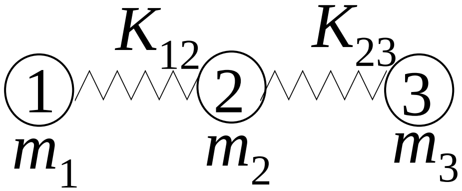
angular frequency

$$\omega_{\mathrm{T}} = \sqrt{\frac{K_{\mathrm{T}}}{m_{\mathrm{T}}}} \,, \quad \omega_{\mathrm{V}} = \sqrt{\frac{K_{\mathrm{V}}}{m_{\mathrm{V}}}}$$

cf.

$$\omega_0 = 0 \,, \quad \omega_1 = \sqrt{\frac{K}{m^*}} \quad \left(m^* = \frac{1}{\mu_1 + \mu_2} \right)$$

Natural oscillation of a linear triatomic molecule



$$\mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2} = \begin{pmatrix} \mu_1 K_{12} & -\sqrt{\mu_1\mu_2}K_{12} & 0 \\ -\sqrt{\mu_1\mu_2}K_{12} & \mu_2(K_{12}+K_{23}) & -\sqrt{\mu_2\mu_3}K_{23} \\ 0 & -\sqrt{\mu_2\mu_3}K_{23} & \mu_3 K_{23} \end{pmatrix}$$

$$\omega^2 = 0,\ \frac{1}{2}\left\{(\mu_1+\mu_2)K_{12} + (\mu_2+\mu_3)K_{23} \pm \sqrt{\left\{(\mu_1+\mu_2)K_{12} - (\mu_2+\mu_3)K_{23}\right\}^2 + 4\mu_2^2 K_{12}K_{23}}\right\}$$

$m_1 = m_3$

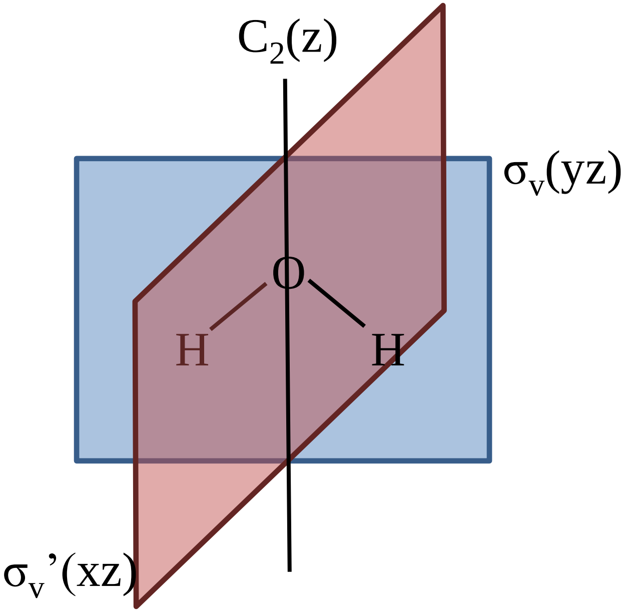
$K_{12} = K_{23} = K$

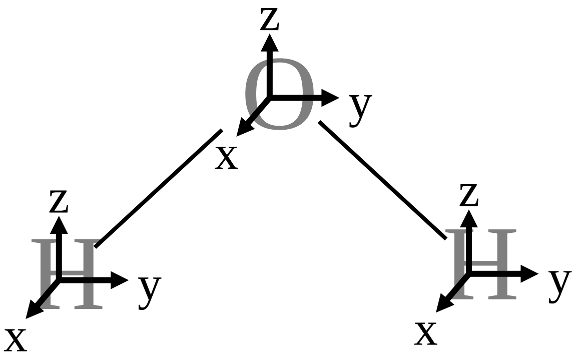
⇨

$$\hat{\mathbf{X}} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & \frac{\mu_1}{\sqrt{2(\mu_1^2+2\mu_2^2)}} \\ \frac{1}{\sqrt{3}} & 0 & -\frac{2\mu_2}{\sqrt{2(\mu_1^2+2\mu_2^2)}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & \frac{\mu_1}{\sqrt{2(\mu_1^2+2\mu_2^2)}} \end{pmatrix}$$

$$\hat{\mathbf{X}}^{\mathrm{T}}\mathbf{M}\hat{\mathbf{X}} = \begin{pmatrix} \frac{2m_1+m_2}{3} & 0 & 0 \\ 0 & m_1 & 0 \\ 0 & 0 & \frac{m_1 m_2(2m_1+m_2)}{2m_1^2+m_2^2} \end{pmatrix} \qquad \hat{\mathbf{X}}^{\mathrm{T}}\mathbf{K}\hat{\mathbf{X}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & K & 0 \\ 0 & 0 & \frac{(\mu_1+2\mu_2)}{\mu_1^2+2\mu_2^2}K \end{pmatrix}$$

13-10 Normal Coordinates Belong to Irreducible Representation of Molecular Point Groups.





C_{2v}	E	C_2	$\sigma_v'(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

C_{2v}	E	C_2	$\sigma_v'(xz)$	$\sigma_v(yz)$
Γ_{3N}	9	-1	1	3

$$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$$

$T_x, T_y, T_z \;\Rightarrow\; B_1, B_2, A_1$
$R_x, R_y, R_z \;\Rightarrow\; B_2, B_1, A_2$
vibrations $\;\Rightarrow\; A_1, A_1, B_2$

13-11 Selection Rules are Derived from Time-dependent Perturbation Theory.

Time-dependent Schrödinger equation: $\hat{H}\Psi = i\hbar\frac{\partial \Psi}{\partial t}, \quad \Psi_n(r,t) = \psi_n(r)\exp\left[-i\frac{E_n t}{\hbar}\right]$

Perturbation from electromagnetic field: $E = E_0 \cos 2\pi \nu t$

$$\hat{H}^{(1)} = -\mu \cdot E = -\mu \cdot E_0 \cos 2\pi \nu t$$

Two-state Model: $\Psi_1(t) = \psi_1 \exp\left[-i\frac{E_1 t}{\hbar}\right], \Psi_2(t) = \psi_2 \exp\left[-i\frac{E_2 t}{\hbar}\right]$

By substituting $\Psi = a_1(t)\Psi_1 + a_2(t)\Psi_2$ into $\hat{H} + \hat{H}^{(1)}\Psi = i\hbar\frac{\partial \Psi}{\partial t}$, we obtain

$$\hat{H}^{(1)}\left(a_1 \exp\left[-i\frac{E_1}{\hbar}t\right]\psi_1 + a_2 \exp\left[-i\frac{E_2}{\hbar}t\right]\psi_2\right)$$

$$= i\hbar\left(\frac{\partial a_1}{\partial t}\right)\exp\left[-i\frac{E_1}{\hbar}t\right]\psi_1 + i\hbar\left(\frac{\partial a_2}{\partial t}\right)\exp\left[-i\frac{E_2}{\hbar}t\right]\psi_2$$

13-11 Selection Rules are Derived from Time-dependent Perturbation Theory. (cont.)

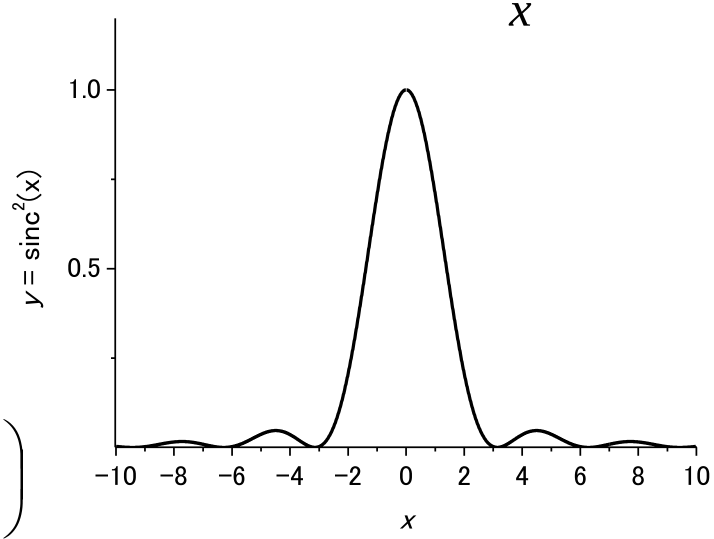
Multiply $\psi_2{}^*$ and integrate over the space. Then, assuming $a_1(0)=1,\ a_2(0)=0$, we obtain :

$$\frac{\partial a_2}{\partial t}=-\frac{i}{\hbar}\exp\left[i\frac{(E_2-E_1)}{\hbar}t\right]\int\psi_2{}^*\hat{H}^{(1)}\psi_1\,\mathrm{d}\tau$$

$$a_2(t)=-\frac{i}{2\hbar}(\mu_z)_{12}E_{0z}\int_0^t\left\{\exp\left[i\frac{(E_2-E_1+h\nu)t'}{\hbar}\right]+\exp\left[i\frac{(E_2-E_1-h\nu)t'}{\hbar}\right]\right\}\mathrm{d}t'$$

$$=\frac{1}{2}(\mu_z)_{12}E_{0z}\left\{\frac{1-\exp\left[-i\frac{(E_2-E_1-h\nu)t}{\hbar}\right]}{E_2-E_1-h\nu}\right\}$$

$$\mathrm{sinc}(x)=\frac{\sin x}{x}$$



Here, the transition dipole moment,

$$(\mu_z)_{12}=\int\psi_2{}^*\mu_z\psi_1\,\mathrm{d}\tau$$

was defied.

$$a_2{}^*(t)a_2(t)=\frac{\left|(\mu_z)_{12}\right|^2E_{0z}{}^2t^2}{4\hbar^2}\mathrm{sinc}^2\left(\frac{(E_2-E_1-h\nu)t}{2\hbar}\right)$$

13-12 The selection rule in the Rigid Rotor Approximation is $\Delta J = \pm 1$.

$$(\mu_z)_{J,M;J',M'} = \int\int Y_J^M(\theta,\phi)\,\hat{\mu}_z\,Y_{J'}^{M'}(\theta,\phi)\sin\theta\ \mathrm{d}\theta\mathrm{d}\phi$$

$$\hat{\mu}_z = \mu\cos\theta$$

$$\Rightarrow \quad M' = M,\ J' = J+1 \text{ or } J-1$$

$$\Rightarrow \quad \Delta M = 0,\ \Delta J = \pm 1$$

13-13 The Harmonic Oscillator Selection Rule is $\Delta v = \pm 1$.

$$(\mu_z)_{\upsilon,\upsilon'} = \int N_\upsilon N_{\upsilon'}\,H_{\upsilon'}(\alpha^{1/2}q)e^{-\alpha q^2/2}\hat{\mu}_z\,H_\upsilon(\alpha^{1/2}q)e^{-\alpha q^2/2}\ \mathrm{d}q$$

$$\mu_z = eq$$

$$\Rightarrow \quad \upsilon' = \upsilon+1,\ \upsilon-1$$

$$\Rightarrow \quad \Delta\upsilon = \pm 1$$

13-14 Group Theory is Used to Determine the Infrared Activity of Normal Coordinate Vibrations Problems

$$I_{0\to 1} = \int \underline{\psi_0(Q_1, Q_2, \cdots Q_{3N-6})}\boxed{\hat{\mu}_z}\underline{\psi_1(Q_1, Q_2, \cdots Q_{3N-6})}\ \mathrm{d}Q_1\mathrm{d}Q_2 \cdots \mathrm{d}Q_{3N\text{-}6}$$

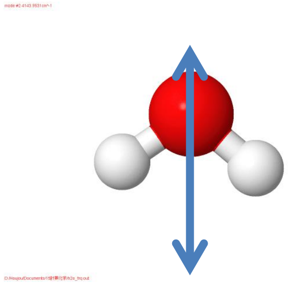
Ground state
（totally symmetric)
A_1

Excited state
(Symmetry depends on normal mode)

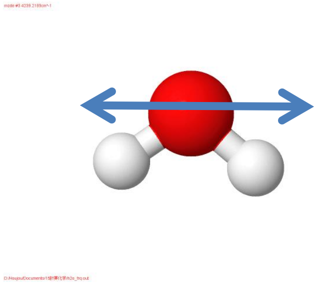
$\mu_x,\ \mu_y,\ \mu_z \Rightarrow B_1, B_2, A_1$

Combination table for water case:

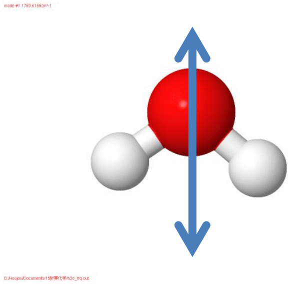
	A_1 (sym. Stretch)	B_2 (asym. Stretch)	A_1 (bend)
B_1 (μ_x)	B_1	A_2	B_1
B_2 (μ_y)	B_2	$\bigcirc A_1$	B_2
A_1 (μ_z)	$\bigcirc A_1$	B_2	$\bigcirc A_1$



A_1 3650 cm^{-1}



B_2 3760 cm^{-1}



A_1 1600 cm^{-1}

18. Partition Function and Ideal Gases

Boltzmann factor: describes a probability that a system in a state of energy E_j.

$$f_j \propto \exp\left[-\frac{E_j}{k_\mathrm{B}T}\right]$$

k_B: Boltzmann constant

Partition function Q: $f_j = \frac{1}{Q}\exp\left[-\frac{E_j}{k_\mathrm{B}T}\right]$, where $Q = \sum_j \exp\left[-\frac{E_j}{k_\mathrm{B}T}\right]$

Boltzmann statistics defines: $Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$

$$q(V,T) = \sum_j \exp\left[-\frac{\varepsilon_j}{k_\mathrm{B}T}\right]$$

Average energy:

$$\langle \varepsilon \rangle = \frac{\sum_j \varepsilon_j \exp\left[-\frac{\varepsilon_j}{k_\mathrm{B}T}\right]}{\sum_j \exp\left[-\frac{\varepsilon_j}{k_\mathrm{B}T}\right]} = k_\mathrm{B}T^2\left(\frac{\partial \ln q}{\partial T}\right)_V$$

18-1 The Translational Partition Function of Monoatomic Ideal Gas is $(2\pi m k_B T/h^2)^{3/2} V$.

Atomic energy of monoatomic ideal gas:

$$\varepsilon_{\text{atomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{elec}}$$

$$q(V,T) = q_{\text{trans}}(V,T)\, q_{\text{elec}}(T)$$

Translational energy state in a cubic container:

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}({n_x}^2 + {n_y}^2 + {n_z}^2) \qquad n_x, n_y, n_z = 1, 2, \cdots$$

$$q_{\text{trans}} = \sum_{n_x, n_y, n_z = 1}^{\infty} \exp\left[-\beta \varepsilon_{n_x n_y n_z}\right] = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{\beta h^2}{8ma^2}({n_x}^2 + {n_y}^2 + {n_z}^2)\right]$$

$$= \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right]^3 \cong \left[\int_0^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) \mathrm{d}n\right]^3$$

$$= \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$$

Average energy

$$\langle \varepsilon_{\text{trans}} \rangle = k_{\text{B}} T^2 \left(\frac{\partial \ln q_{\text{trans}}}{\partial T}\right)_V = \cdots = \frac{3}{2} k_{\text{B}} T$$

18-2 Most of Atoms are in the Ground Electronic State at Room Temperature.

Electronic partition function: $q_{\text{elec}} = \sum_i q_{\text{e}i} \exp(-\beta \varepsilon_{\text{e}i})$

$$q_{\text{elec}}(T) = q_{\text{e1}} + q_{\text{e2}} \exp(-\beta \varepsilon_{\text{e2}}) + \cdots$$

Normally... $\beta \varepsilon_{\text{e}i} = \dfrac{10000\,\text{cm}^{-1}}{0.6950\,\text{cm}^{-1}\,\text{K}} \dfrac{1}{T} \cong \dfrac{10^4\,\text{K}}{T}$ $\Rightarrow$ second or later terms are (often) negligible.

ex.) Ratio of helium atoms in $^3\text{S}_1$ state (1s2s) $^3\text{S}_1 - {}^1\text{S}_0 = 159850.318\ \text{cm}^{-1}$

$$f_2 = \frac{3\exp(-\beta\varepsilon_{\text{e2}})}{1 + 3\exp(-\beta\varepsilon_{\text{e2}}) + \exp(-\beta\varepsilon_{\text{e3}})} = \begin{cases} 10^{-334} & (T = 300\,\text{K}) \\ 10^{-33} & (T = 3000\,\text{K}) \end{cases}$$

Average energy $U = k_\text{B} T^2 \left(\dfrac{\partial \ln Q}{\partial T} \right)_{N,V} = \dfrac{3}{2} k_\text{B} T + \dfrac{N g_{\text{e2}} \varepsilon_{\text{e2}} \exp(-\beta \varepsilon_{\text{e2}})}{q_{\text{elec}}} + \cdots$

Heat capacity $\overline{C}_\text{V} = \left(\dfrac{\text{d}U}{\text{d}T} \right)_{N,V} = \dfrac{3}{2} R$

Pressure $P = k_\text{B} T \left(\dfrac{\partial \ln Q}{\partial V} \right)_{N,T} = \dfrac{N k_\text{B} T}{V}$ (state equation of ideal gas)

18-3 The energy of a Diatomic Molecule can be Approximated as a Sum of Separate Terms.

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}}$$

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$$q_{\text{trans}} = \left[\frac{2\pi(m_1+m_2)k_{\text{B}}T}{h^2}\right]^{3/2}$$

baseline of q_{rot} $\Rightarrow$ $J = 0$
baseline of q_{vib} $\Rightarrow$ $\upsilon = 0$, bottom of potential
baseline of q_{elec} $\Rightarrow$ bottom of potential

18-4 Most Molecules are in the Ground Vibrational State.

Harmonic oscillator approximation:

$$\varepsilon_\upsilon = \left(\upsilon + \frac{1}{2}\right)h\nu$$

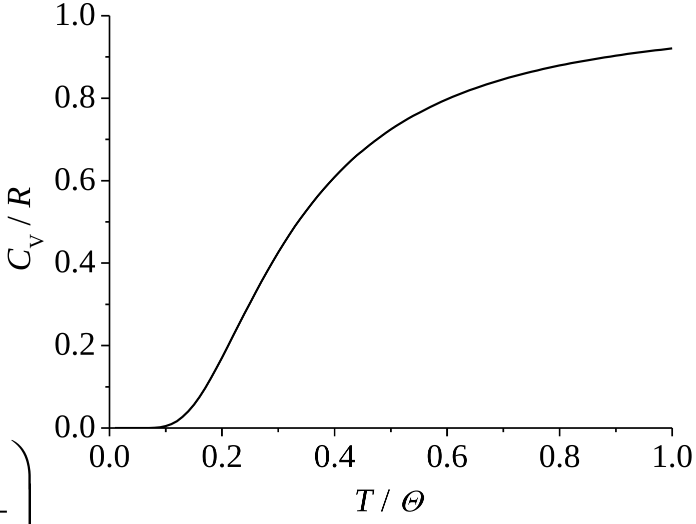
$$q_{\text{vib}}(T) = \sum_\upsilon \exp(-\beta\varepsilon_\upsilon) = \sum_\upsilon^\infty \exp\left[-\beta\left(\upsilon+\frac{1}{2}\right)h\nu\right]$$

$$= \exp\left(-\beta\frac{h\nu}{2}\right)\sum_\upsilon^\infty \exp(-\beta h\nu\upsilon) = \frac{\exp\left(-\beta\frac{h\nu}{2}\right)}{1-\exp(-\beta h\nu)}$$

18-4 Most Molecules are in the Ground Vibrational State. (cont.)

Vibrational Temperature: $\Theta_{\text{vib}} = \dfrac{h\nu}{k_{\text{B}}}$

$$q_{\text{vib}}(T) = \frac{\exp\left(-\Theta_{\text{vib}}/2T\right)}{1-\exp\left(-\Theta_{\text{vib}}/T\right)}$$



Energy

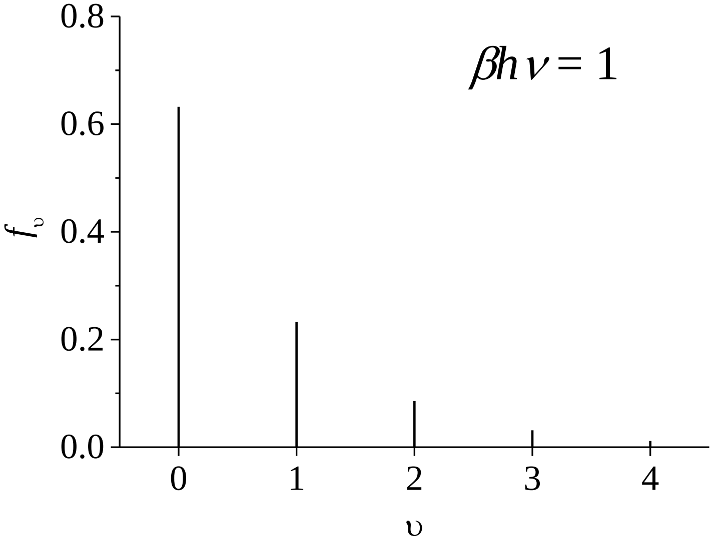
$$\left\langle E_{\text{vib}}\right\rangle = Nk_{\text{B}}T^2\,\frac{\mathrm{d}\ln q_{\text{vib}}}{\mathrm{d}T} = Nk_{\text{B}}\left(\frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{\exp\left(-\Theta_{\text{vib}}/T\right)-1}\right)$$

Heat Capacity

$$C_{V,\text{vib}} = \frac{\mathrm{d}\left\langle E_{\text{vib}}\right\rangle}{\mathrm{d}T} = R\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{\exp\left(-\Theta_{\text{vib}}/T\right)}{\left[1-\exp\left(-\Theta_{\text{vib}}/T\right)\right]^2}$$

Probability of vibrational excitation

$$f_\upsilon = \frac{\exp\left(-\beta h\nu\left(\upsilon+\frac{1}{2}\right)\right)}{q_{\text{vib}}}$$



18-5 Most Molecules are in Excited Rotational States.

Energy level of rigid rotor: $\varepsilon_J = \dfrac{\hbar^2 J(J+1)}{2I} \quad (J = 0, 1, 2, \cdots)$

degeneracy $g_J = 2J + 1$

Partition function: $q_{\mathrm{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\beta \dfrac{\hbar^2 J(J+1)}{2I} \right]$

Rotation Temperature: $\Theta_{\mathrm{rot}} = \dfrac{\hbar^2}{2Ik_{\mathrm{B}}} = \dfrac{hB}{k_{\mathrm{B}}} \qquad q_{\mathrm{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\Theta_{\mathrm{rot}} \dfrac{J(J+1)}{T} \right]$

At ambient temperature, Θ_{rot}/T is small.

$$q_{\mathrm{rot}}(T) = \int_0^{\infty} (2J+1) \exp\left[-\Theta_{\mathrm{rot}} \frac{J(J+1)}{T} \right] \mathrm{d}J$$

(high temperature approximation)

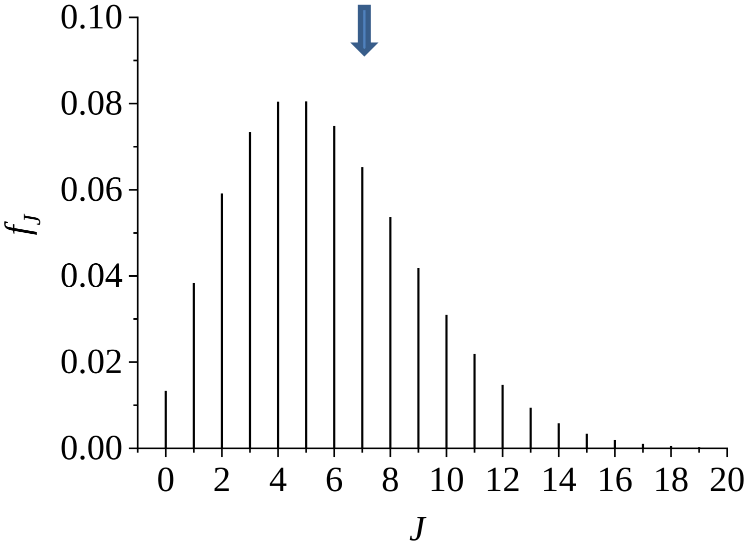
$$= \frac{T}{\Theta_{\mathrm{rot}}} = \frac{8\pi^2 I k_{\mathrm{B}} T}{h^2}$$

Average rotational energy:

$$\langle E_{\mathrm{rot}} \rangle = N k_{\mathrm{B}} T^2 \frac{\mathrm{d} \ln q_{\mathrm{rot}}}{\mathrm{d}T} = N k_{\mathrm{B}} T$$

(rigid rotor
⇒ degree of freedom is 2)

18-5 Most Molecules are in Excited Rotational States. (cont.)



most probable value $\sim \left(\dfrac{T}{\Theta_{\mathrm{rot}}} \right)^{1/2} - \dfrac{1}{2}$

$J = 7$ for CO at 300 K

This determines the profile of P- and R-branches of rotational spectrum.

18-6 Rotational Partition Functions Contain a Symmetry Number.

Homonuclear diatomic molecule $q_{\mathrm{rot}}(T) = \dfrac{T}{2\Theta_{\mathrm{rot}}}$

Heteronuclear diatomic molecule $q_{\mathrm{rot}}(T) = \dfrac{T}{\Theta_{\mathrm{rot}}}$

In summary $q(V,T) = q_{\mathrm{trans}} q_{\mathrm{rot}} q_{\mathrm{vib}} q_{\mathrm{elec}}$

$$= \left[\frac{2\pi M k_{\mathrm{B}} T}{h^2} \right]^{3/2} V \frac{T}{\sigma \Theta_{\mathrm{rot}}} \frac{\exp\left[-\Theta_{\mathrm{vib}}/2T\right]}{1-\exp\left[-\Theta_{\mathrm{vib}}/T\right]} g_{\mathrm{el}} \exp\left[D_{\mathrm{e}}/k_{\mathrm{B}}T\right]$$

18-7 The Vibrational Partition Function of a Polyatomic Molecule is a Product of Harmonic Oscillator Partition Functions for Each Normal Coordinate.

$$q_{\text{vib}} = \prod_{j=1}^{\alpha} \frac{\exp\left[-\Theta_{\text{vib},j}/2T\right]}{1-\exp\left[-\Theta_{\text{vib},j}/T\right]}$$

$$\Theta_{\text{vib},j} = \frac{h\nu_j}{k_{\text{B}}}$$ eigenfrequency temperature

$$\alpha = \begin{cases} 3N-5 & \text{linear molecule} \\ 3N-6 & \text{nonlinear molecule} \end{cases}$$

$$\langle E_{\text{vib}} \rangle = Nk_{\text{B}} \sum_{j}^{\alpha} \left(\frac{\Theta_{\text{vib},j}}{2} + \frac{\Theta_{\text{vib},j}}{\exp\left(\Theta_{\text{vib},j}/T\right)-1} \right)$$

$$C_{\text{V,vib}} = \frac{\mathrm{d}\langle E_{\text{vib}} \rangle}{\mathrm{d}T} = Nk_{\text{B}} \sum_{j}^{\alpha} \left(\left(\frac{\Theta_{\text{vib},j}}{2} \right)^2 \frac{\exp\left(-\Theta_{\text{vib},j}/T\right)}{\left[\exp\left(-\Theta_{\text{vib},j}/T\right)-1\right]^2} \right)$$

18-8 The Form of the Rotational Partition Function of a polyatomic Molecule Depends Upon the Shape of the Molecule.

For linear molecules

$$q_{\text{rot}}(T) = \frac{8\pi^2 I k_{\text{B}} T}{\sigma h^2} = \frac{T}{\sigma \Theta_{\text{rot}}}$$

σ: symmetry number

For non-linear molecules

$$q_{\text{rot}}(T) = \begin{cases} \dfrac{\sqrt{\pi}}{\sigma}\left(\dfrac{T}{\Theta_{\text{rot}}}\right)^{3/2} & \text{spherical top } (I_{\text{A}} = I_{\text{B}} = I_{\text{C}}) \\ \dfrac{\sqrt{\pi}}{\sigma}\left(\dfrac{T}{\Theta_{\text{rot,A}}}\right)\left(\dfrac{T}{\Theta_{\text{rot,C}}}\right)^{1/2} & \text{symmetrical top } (I_{\text{A}} = I_{\text{B}} < I_{\text{C}}) \\ \dfrac{\sqrt{\pi}}{\sigma}\left(\dfrac{T^3}{\Theta_{\text{rot,A}}\Theta_{\text{rot,B}}\Theta_{\text{rot,C}}}\right)^{1/2} & \text{asymmetrical top } (I_{\text{A}} < I_{\text{B}} < I_{\text{C}}) \end{cases}$$

where $\Theta_{\text{rot},j} = \dfrac{\hbar^2}{2I_j k_{\text{B}}}$ is eigenrotational temperature (j = A, B, C).

Average molar rotational energy $U_{\text{rot}} = N_{\text{A}} k_{\text{B}} T^2 \dfrac{\mathrm{d}\ln q_{\text{rot}}(T)}{\mathrm{d}T} = \dfrac{3RT}{2}$

Heat capacity $\overline{C}_{\text{V, rot}} = \dfrac{3R}{2}$

18-9 Calculated Molar Heat Capacities are in Very Good Agreement with Experimental Data.

Linear polyatomic molecule (ideal gas)

$$q(V,T)=\left[\frac{2\pi M k_{\mathrm{B}}T}{h^2}\right]^{3/2} V\,\frac{T}{\sigma\Theta_{\mathrm{rot}}}\left(\prod_{j}^{3N-5}\frac{\exp\left[-\Theta_{\mathrm{vib},j}/2T\right]}{1-\exp\left[-\Theta_{\mathrm{vib},j}/T\right]}\right)g_{\mathrm{el}}\exp\left[-\frac{D_{\mathrm{e}}}{k_{\mathrm{B}}T}\right]$$

$$\frac{U}{Nk_{\mathrm{B}}T}=\frac{3}{2}+\frac{2}{2}+\sum_{j}^{3N-5}\left(\frac{\Theta_{\mathrm{vib},j}}{2T}+\frac{\Theta_{\mathrm{vib},j}/T}{\exp\left(-\Theta_{\mathrm{vib},j}/T\right)-1}\right)-\frac{D_{\mathrm{e}}}{k_{\mathrm{B}}T}$$

$$\frac{C_{\mathrm{V}}}{Nk_{\mathrm{B}}}=\frac{3}{2}+\frac{2}{2}+\sum_{j}^{3N-5}\left(\left(\frac{\Theta_{\mathrm{vib},j}}{T}\right)^2\frac{\exp\left(-\Theta_{\mathrm{vib},j}/T\right)}{\left[\exp\left(-\Theta_{\mathrm{vib},j}/T\right)-1\right]^2}\right)$$

18-9 Calculated Molar Heat Capacities are in Very Good Agreement with Experimental Data. (cont.)

Non-linear polyatomic molecule (ideal gas)

$$q(V,T) = \left[\frac{2\pi M k_\mathrm{B} T}{h^2}\right]^{3/2} V \frac{\sqrt{\pi}}{\sigma}\left(\frac{T^3}{\Theta_\mathrm{rot,A}\Theta_\mathrm{rot,B}\Theta_\mathrm{rot,C}}\right)^{1/2}$$

$$\times\left(\prod_{j=1}^{3N-6}\frac{\exp\left[-\Theta_{\mathrm{vib},j}/2T\right]}{1-\exp\left[-\Theta_{\mathrm{vib},j}/T\right]}\right) g_\mathrm{el}\exp\left[-\frac{D_\mathrm{e}}{k_\mathrm{B}T}\right]$$

$$\frac{U}{Nk_\mathrm{B}T} = \frac{3}{2}+\frac{3}{2}+\sum_{j}^{3N-6}\left(\frac{\Theta_{\mathrm{vib},j}}{2T}+\frac{\Theta_{\mathrm{vib},j}/T}{\exp\left(-\Theta_{\mathrm{vib},j}/T\right)-1}\right)-\frac{D_\mathrm{e}}{k_\mathrm{B}T}$$

$$\frac{C_\mathrm{V}}{Nk_\mathrm{B}} = \frac{3}{2}+\frac{3}{2}+\sum_{j=1}^{3N-6}\left(\left(\frac{\Theta_{\mathrm{vib},j}}{T}\right)^2\frac{\exp\left(-\Theta_{\mathrm{vib},j}/T\right)}{\left[\exp\left(-\Theta_{\mathrm{vib},j}/T\right)-1\right]^2}\right)$$

Molar heat capacity（300 K）

	C_V/R calcd.	C_V/R exptl.
CO_2	3.49	3.46
CH_4	3.30	3.29
H_2O	3.03	3.01

20. Entropy and the Second Law of Thermodynamics

20-1 The Change of Energy Alone is not Sufficient to Determine the Direction of a Spontaneous Process.

Spontaneously processing chemical reactions ⇒ always exothermic?

Diffusion of a gas: ΔU and ΔH are nearly 0 ⇒ but retrogression never happens.

Examples: mixing of gases, fusion of ice, reaction of $Ba(OH)_2$ and NH_4NO_3, etc.

20-2 Nonequilibrium Isolated Systems Evolve in a Direction that Increases Their Disorder.

Spontaneous process → Disorder of the system increases.

↓

*tendency for energy to be minimized
*tendency for disorder to be maximized

The first law tells: $\delta q_{\text{rev}} = \mathrm{d}U - \delta W = C_{\text{V}}(T)\,\mathrm{d}T + P\,\mathrm{d}V$

$$= C_{\text{V}}(T)\,\mathrm{d}T + \frac{nRT}{V}\mathrm{d}V \quad \cdots$$

This is not an exact differential.
(for q_{rev} depends on paths of integration)

20-2 Nonequilibrium Isolated Systems Evolve in a Direction that Increases Their Disorder. (cont.)

$$C_\mathrm{V}(T)\,\mathrm{d}T = \mathrm{d}\int C_\mathrm{V}(T)\,\mathrm{d}T + const.$$

$$\frac{nRT}{V}\,\mathrm{d}V \neq \mathrm{d}\int \frac{nRT}{V}\,\mathrm{d}V + const.$$

T depends on *V*.

By dividing by *T*, this gives:

$$\begin{aligned}\frac{\delta q_\mathrm{rev}}{T} &= \frac{C_\mathrm{V}(T)}{T}\,\mathrm{d}T + \frac{nR}{V}\,\mathrm{d}V \\ &= \mathrm{d}S\end{aligned}$$

S: entropy

$$\oint \mathrm{d}S = 0$$

S is a state function.

20-3 Unlike q_{rev}, Entropy is a State Function

● $\delta q_{\mathrm{rev,A}} = \dfrac{nRT_1}{V}\,\mathrm{d}V$

● $\delta q_{\mathrm{rev,B}} = 0$

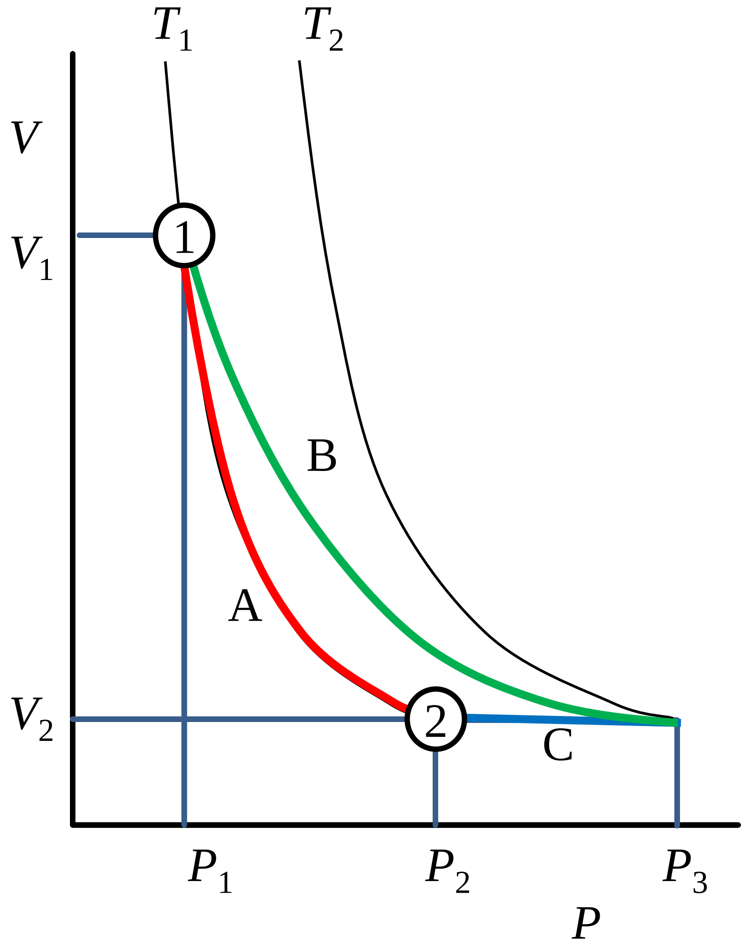
● $\delta q_{\mathrm{rev,C}} = C_{\mathrm{V}}(T)\,\mathrm{d}T$

$$\Rightarrow q_{\mathrm{rev,A}} = nRT_1 \ln\frac{V_2}{V_1} \qquad \Rightarrow q_{\mathrm{rev,B+C}} = \int_{T_1}^{T_2} C_{\mathrm{V}}(T)\,\mathrm{d}T$$

$$\textit{in process B,}\quad \Delta U = \mathrm{d}w = -nRT/V\,\mathrm{d}V$$

$$\Rightarrow \int_{T_1}^{T_2} \frac{C_{\mathrm{V}}(T)}{T}\,\mathrm{d}T = -nR\ln\frac{V_2}{V_1}$$

$$\Delta S = \int_1^2 \frac{\delta q_{\mathrm{rev}}}{T} \quad \text{is independent of the path}$$



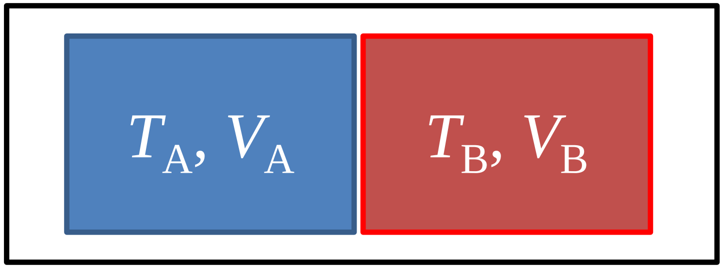
● $\Delta S_{\mathrm{A}} = nR\ln\dfrac{V_2}{V_1}$

$$\left.\begin{aligned} &● \quad \Delta S_{\mathrm{B}} = 0 \\ &● \quad \Delta S_{\mathrm{C}} = -\int_{T_1}^{T_2} \frac{C_{\mathrm{V}}(T)}{T}\,\mathrm{d}T \end{aligned}\right\} \Delta S_{\mathrm{B+C}} = 0 + nR\ln\frac{V_2}{V_1} = \Delta S_{\mathrm{A}}$$

As temperature goes lower, the disorder of a system by δq_{rev} is larger.

20-4 The Second Law of Thermodynamics States that the Entropy of an Isolated System Increases as a Result of Spontaneous Process.

Thermal energy: spontaneously moves from high-T region to low-T region (observed fact).



$U_A + U_B$ = const.
V_A = const., V_B = const.
$S = S_A + S_B$

$$\left.\begin{aligned} dU_A &= \delta q_{rev} + \delta w_{rev} = T_A\, dS_A \\ dU_B &= \delta q_{rev} + \delta w_{rev} = T_B\, dS_B \end{aligned}\right\} \Rightarrow dS = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$$

$$dU_A = -dU_B$$

$$dS = dU_B\left(\frac{1}{T_B} - \frac{1}{T_A}\right)$$

If $T_B > T_A$, $dU_B < 0$, therefore $dS > 0$
At equilibrated state, $dS = 0$

$$dS = dS_{prod} + dS_{exch} = dS_{prod} + \frac{\delta q}{T} \geq \frac{\delta q}{T}$$

dS_{prod}: produced inside the system (≥ 0)
dS_{exch}: given by heat exchange ($\delta q/T$)

$$\Delta S \geq \int \frac{\delta q}{T} \quad \text{(the Inequality of Clausius)}$$

20-5 The Most Famous Equation of Statistical Thermodinamics is $S = k_B \ln W$

Ensemble of A pieces of isolated systems

Energy E (degeneracy $\Omega(E)$) → $j = 1, 2, \cdots \Omega(E)$

Volume V

Number of particles N


a_1 a_2 a_3 a_4 $\cdots$ $a_{\Omega(E)}$

Number of isolated systems in jth state = a_j $\quad \sum_j a_j = A$

$$\text{Number of Ways:}\quad W(a_1, a_2, \cdots a_\Omega)! = \frac{A!}{a_1! a_2! \cdots a_\Omega!} = \frac{A!}{\prod_j a_j!}$$

$$\text{Entropy:}\quad S = k_B \ln W$$

$$\Leftrightarrow \begin{cases} S_{\text{total}} = S_A + S_B \\ W_{AB} = W_A W_B \end{cases}$$

S is maximized in equilibrated system. ⇒ W is max. ⇒ All the n are the same.

$$\forall j, a_j = n \;\Rightarrow\; A = n\Omega$$

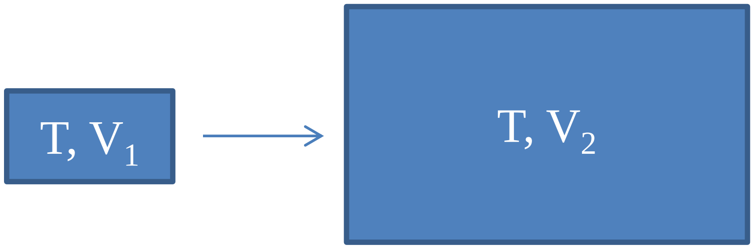
$$S_{\text{ensemble}} = k_B \ln W = k_B \left[A \ln A - \sum_{j=1}^{\Omega} a_j \ln a_j \right] = k_B \left[n\Omega \ln n\Omega - \sum_{j=1}^{\Omega} n \ln n \right] = k_B (n\Omega \ln \Omega)$$

$$\because \ln N! \cong N \ln N - N \quad \text{(Stirling's formula)}$$

$$S_{\text{ensemble}} = n\Omega S_{\text{system}} \Rightarrow S_{\text{system}} = k_B \ln \Omega$$

20-6 We must Always Devise a Reversible Process to Calculate Entropy Changes.

ex.1 Free expansion of gas
(isothermal process)


T, V_1 → T, V_2

$$\Delta S = \int_1^2 \frac{\delta q_{\mathrm{rev}}}{T}$$

$$\delta q_{\mathrm{rev}} = -\delta w_{\mathrm{rev}} = P\mathrm{d}V = \frac{nRT}{V}\mathrm{d}V \qquad \Delta S = nR\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V} = nR\ln\frac{V_2}{V_1}$$

ex.2 At the interface of metal pieces of different temperature...

Energy: $C_V(T_h - T) = C_V(T - T_c) \Rightarrow T = \dfrac{T_h + T_c}{2} \Rightarrow \Delta S = \displaystyle\int_{T_1}^{T_2}\frac{C_V}{T}\mathrm{d}T = C_V\ln\frac{T_2}{T_1}$

Entropy:

High-T side $\quad \Delta S_h = C_V \ln\dfrac{T_h + T_c}{2T_h}$

Low-T side $\quad \Delta S_c = C_V \ln\dfrac{T_h + T_c}{2T_c}$

total change in entropy

$$\left.\begin{aligned}\Delta S_h &= C_V \ln\frac{T_h + T_c}{2T_h}\\ \Delta S_c &= C_V \ln\frac{T_h + T_c}{2T_c}\end{aligned}\right\} \Rightarrow \Delta S = \Delta S_h + \Delta S_c = C_V \ln\frac{(T_h + T_c)^2}{4T_hT_c}$$

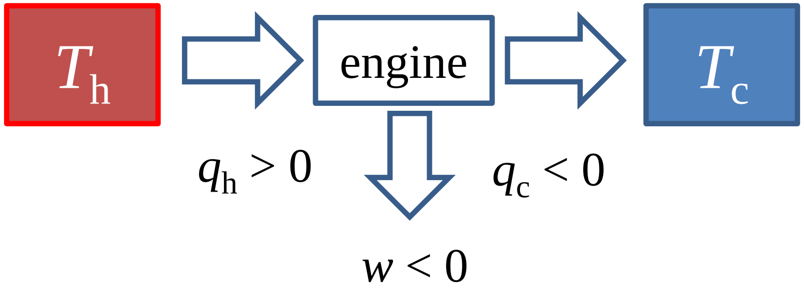
$(T_h + T_c)^2 > 4T_hT_c$, therefore $\quad \Delta S > 0$

20-7 Thermodynamics Gives Us Insight into the Conversion of Heat into Work.

$$\Delta U_{\text{engine}} = w + q_{\text{rev,h}} + q_{\text{rev,c}} = 0$$

$$\Delta S_{\text{engine}} = \frac{\delta q_{\text{rev,h}}}{T_{\text{h}}} + \frac{\delta q_{\text{rev,c}}}{T_{\text{c}}} = 0 \qquad \text{(reversible)}$$

$$-w = q_{\text{rev,h}} + q_{\text{rev,c}}$$



$$\text{Max efficiency} \quad \eta_{\max} = \frac{-w}{q_{\text{rev,h}}} = \frac{q_{\text{rev,h}} + q_{\text{rev,c}}}{q_{\text{rev,h}}} = 1 - \frac{T_{\text{c}}}{T_{\text{h}}} = \frac{T_{\text{h}} - T_{\text{c}}}{T_{\text{h}}} \quad \leftarrow \text{depends only on } T.$$

20-8 Entropy can be Expressed in Terms of a Partition Function.

$$U = k_{\text{B}}T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} \qquad \because \frac{\text{d}\beta}{\text{d}T} = -\frac{1}{k_{\text{B}}T^2}$$

$$P = k_{\text{B}}T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$S_{\text{ensemble}} = k_{\text{B}} \ln \frac{\mathcal{A}!}{\prod_j a_j!} \simeq k_{\text{B}}\left[\mathcal{A} \ln \mathcal{A} - \sum_{j=1}^{\Omega} a_j \ln a_j\right] = \mathcal{A} S_{\text{system}}$$

20-8 Entropy can be Expressed in Terms of a Partition Function. (cont.)

Probability that the state of the system is *j*: $p_j = \dfrac{a_j}{\mathcal{A}}$

$$S_{\text{ensemble}} = -\mathcal{A} k_{\mathrm{B}} \sum_j p_j \ln p_j \ \Rightarrow\ S_{\text{system}} = -k_{\mathrm{B}} \sum_j p_j \ln p_j$$

$$p_j = p_j(N,V,\beta) = \frac{\exp\left[-\beta E_j(N,V)\right]}{Q(N,V,\beta)}$$

then,

$$S_{\text{system}} = -k_{\mathrm{B}} \sum_j \frac{\exp\left[-\beta E_j\right]}{Q}(-\beta E_j - \ln Q) = \frac{U}{T} + k_{\mathrm{B}} \ln Q = k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_{\mathrm{B}} \ln Q$$

Monoatomic ideal gas
in the ground state:

$$Q = Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3N/2} V^N g_{\text{el}}$$

Entropy per 1 mol:

$$\bar{S} = \frac{3}{2} R + R \ln\left[\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2} \bar{V} g_{\text{el}}\right] - k_{\mathrm{B}} \ln N_{\mathrm{A}}!$$

$$= \frac{5}{2} R + R \ln\left[\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2} \frac{\bar{V} g_{\text{el}}}{N_{\mathrm{A}}}\right]$$

20-9 The Molecular Formula $S = k_B \ln W$ is Analogous to Thermodynamic Formula $dS = \delta q_{rev} / T$.

$$S = -k_B \sum_j p_j \ln p_j$$

By differentiating by p_j, $$dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$$

$\sum_j dp_j = 0$, therefore $$dS = -k_B \sum_j \ln p_j dp_j$$

By substituting $\ln p_j$ with $p_j = \dfrac{\exp[-\beta E_j]}{Q}$,

$$dS = -k_B \sum_j [-\beta E_j - \ln Q] dp_j$$

$$\sum_j [\ln Q] dp_j = \ln Q \sum_j dp_j = 0$$

then, $$dS = -\beta k_B \sum_j E_j dp_j$$

$\sum_j E_j dp_j$ is energy transferred among the system as heat during a reversible process.

$$\Rightarrow dS = -\beta k_B \delta q_{rev} = \frac{\delta q_{rev}}{T}$$

1．多原子分子の形状をその慣性主値にもとづいて球対称、扁平対称、扁長対称に分類し、量子化された回転運動エネルギーとの関係をわかりやすく説明せよ。全角運動量量子数$J = 2$とする。

2．質量換算Hessian法によって基準振動モードを解析する手順について、CO_2の分子軸方向の原子変位を例にとって説明せよ。C=O結合をばねと見做した時の力の定数をkとし、2個の基準振動モードのモード質量とモード剛性を明示せよ。

3．H_2O分子の三種の分子内振動モードは、それぞれどの向きの偏光によって励起されるか。C_{2v}点群における既約表現と遷移双極子モーメントの考え方に基づいて説明せよ。

4．単原子分子を例にとり、並進運動のエネルギー表式から出発して理想気体の状態方程式を導出せよ。

26. Chemical Equilibrium

26-1 Chemical Equilibrium Results When the Gibbs Energy is a Minimum with Respect to the Extent of Reaction

Gas phase reaction $\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g)$

Extent of reaction ξ

$$\mathrm{d}n_A = -\nu_A \mathrm{d}\xi \qquad \mathrm{d}n_Y = \nu_Y \mathrm{d}\xi$$

$$\mathrm{d}n_B = -\nu_B \mathrm{d}\xi \qquad \mathrm{d}n_Z = \nu_Z \mathrm{d}\xi$$

Chemical potential $\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,n_Z}$

at constant *T*, *P*:

$$\mathrm{d}G = \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \mu_Y \mathrm{d}n_Y + \mu_Z \mathrm{d}n_Z$$

$$= (-\nu_A\mu_A - \nu_B\mu_B + \nu_Y\mu_Y + \nu_Z\mu_Z)\mathrm{d}\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\nu_A\mu_A - \nu_B\mu_B + \nu_Y\mu_Y + \nu_Z\mu_Z \equiv \Delta_r G$$

in equilibrium, $\Delta_r G = 0$

$$\Delta_r G^\circ(T) = -RT \ln K_P(T) \qquad K_P(T) = \left(\frac{P_Y{}^{\nu_Y} P_Z{}^{\nu_Z}}{P_A{}^{\nu_A} P_B{}^{\nu_B}}\right)_{eq}$$

(equilibrium constant)

26-2 An Equilibrium Constant is a Function of Temperature Only

$$\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)+Cl_2(g)} \qquad K_P(T)=\left(\frac{P_\mathrm{Y}{}^{\nu_\mathrm{Y}}P_\mathrm{Z}{}^{\nu_\mathrm{Z}}}{P_\mathrm{A}{}^{\nu_\mathrm{A}}P_\mathrm{B}{}^{\nu_\mathrm{B}}}\right)_\mathrm{eq}=\frac{\xi_\mathrm{eq}{}^2}{1-\xi_\mathrm{eq}{}^2}P$$

Equilibrium constant $K_P(T)$ does not depend on a total pressure P, but P controls ξ_eq.
⇒Le Chatelier's principle

conversion from P-representation to c-representation: (P° = 0.1 MPa, c° = 1 mol $\mathrm{L^{-1}}$)

$$K_P=K_c\left(\frac{c^\circ RT}{P^\circ}\right)^{\nu_\mathrm{Y}+\nu_\mathrm{Z}-\nu_\mathrm{A}-\nu_\mathrm{B}} \qquad K_c=\frac{(c_\mathrm{Y}/c^\circ)^{\nu_\mathrm{Y}}(c_\mathrm{Z}/c^\circ)^{\nu_\mathrm{Z}}}{(c_\mathrm{A}/c^\circ)^{\nu_\mathrm{A}}(c_\mathrm{B}/c^\circ)^{\nu_\mathrm{B}}}$$

26-3 Standard Gibbs Energies of Formation can be Used to Calculate Equilibrium Constants

$\Delta_\mathrm{r}H^\circ$ is calculated from standard enthalpy of formation.
$\Delta_\mathrm{r}S^\circ$ is calculated from standard (absolute) entropy.

$$\begin{aligned}\Delta_\mathrm{r}G^\circ &=\Delta_\mathrm{r}H^\circ-T\Delta_\mathrm{r}S^\circ\\ &=\nu_\mathrm{Y}\Delta_\mathrm{f}G^\circ[\mathrm{Y}]+\nu_\mathrm{Z}\Delta_\mathrm{f}G^\circ[\mathrm{Z}]-\nu_\mathrm{A}\Delta_\mathrm{f}G^\circ[\mathrm{A}]-\nu_\mathrm{B}\Delta_\mathrm{f}G^\circ[\mathrm{B}]\end{aligned} \qquad \ln K_P(T)=-\frac{\Delta_\mathrm{r}G^\circ}{RT}$$

26-4 A Plot of the Gibbs Energy of a Reaction Mixture Against the Extent of Reaction is a Minimum at Equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$G(\xi) = (1-\xi)\overline{G}_{N_2O_4} + 2\xi\overline{G}_{NO_2}$$
$$= (1-\xi)G^\circ{}_{N_2O_4} + 2\xi G^\circ{}_{NO_2} + (1-\xi)RT\ln P_{N_2O_4} + 2\xi RT\ln P_{NO_2}$$

When a total pressure is 0.1 MPa ,

$$P_{N_2O_4} = \frac{1-\xi}{1+\xi}, \qquad P_{NO_2} = \frac{2\xi}{1+\xi}$$

$$\Delta_f G^\circ{}_{N_2O_4} = 97.787\,\mathrm{kJ\,mol^{-1}}$$
$$\Delta_f G^\circ{}_{NO_2} = 51.258\,\mathrm{kJ\,mol^{-1}}$$

$$G(\xi) = (1-\xi)\Delta_f G^\circ{}_{N_2O_4} + 2\xi\Delta_f G^\circ{}_{NO_2} + (1-\xi)RT\ln\frac{1-\xi}{1+\xi} + 2\xi RT\ln\frac{2\xi}{1+\xi}$$

Under appropriate standard conditions (RT = 2.4790 kJ mol^{-1}),
$\xi = \xi_{\mathrm{eq}}$ that minimizes $G(\xi)$ leads to the equilibrium constant ⇒ $K_P = 0.148$

This value coincides with that obtained from $\ln K_P(T) = -\dfrac{\Delta_r G^\circ}{RT}$.

26-5 The Ratio of the Reaction Quotient to the Equilibrium Constant Determines the Direction in which a Reaction will Proceed

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

$$\Delta_r G = \Delta_r G^\circ(T) + RT \ln \frac{P_Y{}^{\nu_Y} P_Z{}^{\nu_Z}}{P_A{}^{\nu_A} P_B{}^{\nu_B}}$$ (P is not necessarily equilibrium pressure.)

Reaction Quotient: $$Q_P = \frac{P_Y{}^{\nu_Y} P_Z{}^{\nu_Z}}{P_A{}^{\nu_A} P_B{}^{\nu_B}} \qquad \Delta_r G = RT \ln(Q_P / K_P)$$

$Q_P < K_P \Rightarrow$ Reaction proceeds from left to right spontaneously.
($Q_P > K_P \Rightarrow$ right to left)

26-6 The Sign of $\Delta_r G$ and not that of $\Delta_r G^\circ$ Determines the Direction of Reaction Spontaneity

$\Delta_r G^\circ < 0 \Rightarrow K_P > 1$: Reaction proceeds from left to right.
$\Delta_r G^\circ > 0 \Rightarrow K_P < 1$: Reaction proceeds from right to left.

$\mathrm{N_2O_4(g)} \rightleftharpoons \mathrm{2NO_2(g)}$ $\Delta_r G < 0$: spontaneous (until $Q_P = K_P$)

$\mathrm{2H_2(g) + O_2(g)} \rightleftharpoons \mathrm{2H_2O(g)}$ $\Delta_r G < 0$: No reaction without any initiation.

26-7 The Variation of an Equilibrium Constant with Temperature is Given by the van't Hoff Equation

Gibbs-Helmholtz formula

$$\left(\frac{\partial}{\partial T}\frac{\Delta_{\mathrm{r}}G^{\circ}}{T}\right)_P = -\frac{\Delta_{\mathrm{r}}H^{\circ}}{T^2}$$

By representing Gibbs energy with equilibrium constant

$$\left(\frac{\partial \ln K_P}{\partial T}\right)_P = \frac{\mathrm{d}\ln K_P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{r}}H^{\circ}}{RT^2}$$

$\Delta_{\mathrm{r}}H^{\circ} > 0$（endothermic） high-$T$→high-$K_P$

$\Delta_{\mathrm{r}}H^{\circ} < 0$（exothermic） high-$T$→low-$K_P$

Integration from T_1 to T_2 results:

$$\ln\frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2}\frac{\Delta_{\mathrm{r}}H^{\circ}(T)}{RT^2}\mathrm{d}T = \frac{\Delta_{\mathrm{r}}H^{\circ}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$\ln K_P$ is proportional to $1/T$ (cf. Clausius-Clapeyron equation)

Temperature-dependence of $\Delta_{\mathrm{r}}H$

$$\Delta_{\mathrm{r}}H^{\circ}(T) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \cdots$$

→ conversion into temperature-dependence of K_P

$$\ln K_P(T) = A - \frac{\alpha}{RT} + \frac{\beta}{R}\ln T + \frac{\gamma}{R}T + \frac{\delta}{2R}T^2 + \cdots$$

26-8 We can Calculate Equilibrium Constants in Terms of Partition Functions

Gas phase reaction under constant *V*, *T*

$$\nu_{\mathrm{A}}\mathrm{A(g)}+\nu_{\mathrm{B}}\mathrm{B(g)} \rightleftharpoons \nu_{\mathrm{Y}}\mathrm{Y(g)}+\nu_{\mathrm{Z}}\mathrm{Z(g)}$$

Helmholtz energy: $\mathrm{d}A=\mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}}+\mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}}+\mu_{\mathrm{Y}}\mathrm{d}n_{\mathrm{Y}}+\mu_{\mathrm{Z}}\mathrm{d}n_{\mathrm{Z}}$

Condition for chemical equilibrium: $\nu_{\mathrm{Y}}\mu_{\mathrm{Y}}+\nu_{\mathrm{Z}}\mu_{\mathrm{Z}}-\nu_{\mathrm{A}}\mu_{\mathrm{A}}-\nu_{\mathrm{B}}\mu_{\mathrm{B}}=0$

Partition function of a mixed gas is the product of those for each component.

$$\begin{aligned} Q &= Q(N_{\mathrm{A}},N_{\mathrm{B}},N_{\mathrm{Y}},N_{\mathrm{Z}},V,T) \\ &= Q(N_{\mathrm{A}},V,T)\times Q(N_{\mathrm{B}},V,T)\times\cdots \\ &= \frac{q_{\mathrm{A}}(V,T)^{N_{\mathrm{A}}}}{N_{\mathrm{A}}!}\times\cdots \end{aligned}$$

Chemical potential:

$$\mu_{\mathrm{A}}=-RT\left(\frac{\partial\ln Q}{\partial N_{\mathrm{A}}}\right)_{N_j,V,T}=-RT\ln\frac{q_{\mathrm{A}}(V,T)}{N_{\mathrm{A}}} \qquad (\because A=U-TS=-RT\ln Q)$$

With an equilibrium condition, $\dfrac{N_{\mathrm{Y}}{}^{\nu_{\mathrm{Y}}}N_{\mathrm{Z}}{}^{\nu_{\mathrm{Z}}}}{N_{\mathrm{A}}{}^{\nu_{\mathrm{A}}}N_{\mathrm{B}}{}^{\nu_{\mathrm{B}}}}=\dfrac{q_{\mathrm{Y}}{}^{\nu_{\mathrm{Y}}}q_{\mathrm{Z}}{}^{\nu_{\mathrm{Z}}}}{q_{\mathrm{A}}{}^{\nu_{\mathrm{A}}}q_{\mathrm{B}}{}^{\nu_{\mathrm{B}}}}$ $\Rightarrow$ representation of K_c

26-8 We can Calculate Equilibrium Constants in Terms of Partition Functions (cont.)

A. reaction of diatomic molecules

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons \mathrm{2HI(g)}$$

$$K(T) = \frac{q_{\mathrm{HI}}{}^2}{q_{\mathrm{H_2}} q_{\mathrm{I_2}}}$$

$$= \left(\frac{m_{\mathrm{HI}}{}^2}{m_{\mathrm{H_2}} m_{\mathrm{I_2}}} \right)^{3/2} \left(\frac{4\Theta_{\mathrm{rot}}^{\mathrm{H_2}} \Theta_{\mathrm{rot}}^{\mathrm{I_2}}}{\left(\Theta_{\mathrm{rot}}^{\mathrm{HI}}\right)^2} \right) \frac{\left\{1 - \exp\left[-\Theta_{\mathrm{vib}}^{\mathrm{H_2}}/T\right]\right\}\left\{1 - \exp\left[-\Theta_{\mathrm{vib}}^{\mathrm{I_2}}/T\right]\right\}}{\left\{1 - \exp\left[-\Theta_{\mathrm{vib}}^{\mathrm{HI}}/T\right]\right\}^2} \exp \frac{2D_0^{\mathrm{HI}} - D_0^{\mathrm{H_2}} - D_0^{\mathrm{I_2}}}{RT}$$

On calculating K_P based on the right table,
→to plot against $1/T$
→to derive ΔH from the line slope
Calcd.: -12.9 kJ / mol
Obsd.: -13.4 kJ / mol

T/K	$K_P(T)$	ln $K_P(T)$
500	138	4.92
750	51.1	3.93
1000	28.5	3.35
1250	19.1	2.95
1500	14.2	2.65

B. reaction of polyatomic molecules
to use rotation temperature of asymmetric top
to use vibration temperatures of normal modes

Calculated formation constant of H_2O(g) →

T/K	ln $K_P(T)$ (calcd.)	ln $K_P(T)$ exptl.
1000	23.5	23.3
1500	13.1	13.2
2000	8.52	8.15

26-9 Molecular Partition Functions and Related Thermodynamic Data Are Extensively Tabulated (omitted)

26-10 Equilibrium Constants for Real Gases are Expressed in Terms of Partial Fugacities

Chemical potential of non-ideal gas (introduction of fugacity *f*)

$$\mu(T,P) = \mu^\circ(T) + RT\ln\frac{f}{f^\circ} = \mu^\circ(T) + RT\ln f \qquad \text{relative to standard state } f^\circ$$

gas phase reaction

$$\nu_\mathrm{A}\mathrm{A(g)} + \nu_\mathrm{B}\mathrm{B(g)} \rightleftharpoons \nu_\mathrm{Y}\mathrm{Y(g)} + \nu_\mathrm{Z}\mathrm{Z(g)}$$

At equilibrium condition ($\Delta_\mathrm{r}G = 0$)

$$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\circ + RT\ln\frac{f_\mathrm{Y}^{\nu_\mathrm{Y}} f_\mathrm{Z}^{\nu_\mathrm{Z}}}{f_\mathrm{A}^{\nu_\mathrm{A}} f_\mathrm{B}^{\nu_\mathrm{B}}} = 0 \;\Rightarrow\; \Delta_\mathrm{r}G^\circ = -RT\ln K_f \qquad K_f(T) = \left(\frac{f_\mathrm{Y}^{\nu_\mathrm{Y}} f_\mathrm{Z}^{\nu_\mathrm{Z}}}{f_\mathrm{A}^{\nu_\mathrm{A}} f_\mathrm{B}^{\nu_\mathrm{B}}}\right)_\mathrm{eq}$$

K_f: thermodynamical equilibrium constant

$$\frac{1}{2}\mathrm{N_2(g)} + \frac{3}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{NH_3(g)}$$

P_total/MPa	$K_P/10^{-3}$	$K_f/10^{-3}$
1	6.59	6.55
3	6.76	6.59
5	6.90	6.50
10	7.25	6.36
30	8.84	6.08

26-11 Thermodynamic Equilibrium Constants are Expressed in Terms of Activities

Chemical potential of non-ideal solution (introduction of activity)

$\mu_j = \mu_j^* + RT\ln a_j$ solvent of a dilute solution: $a_j \to x_j$ when $x_j \to 1$

μ_j^* is a chemical potential of pure solvent (Raoult's standard state)

$\mu_j = \mu_j^\circ + RT\ln a_j$ slutes of a dilute solution: $a_j \to c_j$ when $c_j \to 0$

μ_j° is a chemical potential of solute in 1 M ideal solution

(Henry's standard state)

General reaction

$$\nu_\mathrm{A}\mathrm{A} + \nu_\mathrm{B}\mathrm{B} \rightleftharpoons \nu_\mathrm{Y}\mathrm{Y} + \nu_\mathrm{Z}\mathrm{Z}$$

At equilibrium condition ($\Delta_\mathrm{r}G = 0$),

$$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\circ + RT\ln\frac{a_\mathrm{Y}^{\nu_\mathrm{Y}} a_\mathrm{Z}^{\nu_\mathrm{Z}}}{a_\mathrm{A}^{\nu_\mathrm{A}} a_\mathrm{B}^{\nu_\mathrm{B}}} = 0 \;\Rightarrow\; \Delta_\mathrm{r}G^\circ = -RT\ln K_a \qquad K_a(T) = \left(\frac{a_\mathrm{Y}^{\nu_\mathrm{Y}} a_\mathrm{Z}^{\nu_\mathrm{Z}}}{a_\mathrm{A}^{\nu_\mathrm{A}} a_\mathrm{B}^{\nu_\mathrm{B}}}\right)_\mathrm{eq}$$

K_a: thermodynamical equilibrium constant

Calculation of activity

$$\ln a = \frac{1}{RT}\int_1^P \bar{V}\,\mathrm{d}P' \qquad \text{(gas phase)}$$

$$= \frac{\bar{V}}{RT}(P-1) \qquad \text{(condensed phase)}$$

26-12 The Use of Activities Makes a Significant Difference in Solubility Calculations Involving Ionic Species

Dissociation of aqueous acetic acid (0.100 M)

$$\mathrm{CH_3COOH(aq)+H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(g)+CH_3COO^-(aq)}$$

$$K_a = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{CH_3COO^-}}}{a_{\mathrm{CH_3COOH}}a_{\mathrm{H_2O}}} = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{CH_3COO^-}}}{a_{\mathrm{CH_3COOH}}} = 1.74\times10^{-5}$$

$$= \frac{c_{\mathrm{H_3O^+}}c_{\mathrm{CH_3COO^-}}\gamma_\pm^2}{c_{\mathrm{CH_3COOH}}}$$

approx. $\gamma_\pm = 1$ ⇒ $c_{\mathrm{H3O+}} = 1.31$ mM, pH = 2.88

Calculating $\gamma_\pm$ (by Debye-Hückel's limiting law, I_c is ionic strength)

$$\ln\gamma_\pm = -\frac{1.173|z_+z_-|(I_c)^{1/2}}{1+(I_c)^{1/2}} \qquad I_c = \frac{1}{2}(c_{\mathrm{H_3O^+}}+c_{\mathrm{CH_3COO^-}}) = c_{\mathrm{H_3O^+}} = c_{\mathrm{CH_3COO^-}}$$

⇒$c_{\mathrm{H3O+}} = 1.31$ mM as initial value results $\gamma_\pm$, which gives new $c_{\mathrm{H3O+}}$ (iteratively).
⇒ $\gamma_\pm = 0.959$, $c_{\mathrm{H3O+}} = 1.37$ mM, pH = 2.86

More noticeable error occurs in calculating solubility.

For $\mathrm{BaF_2}$: approx. $\gamma_\pm = 1$ ⇒ $s = 7.52\times10^{-3}$ M
iterative method $\gamma_\pm = 0.700$ ⇒ $s = 0.011$ M

基礎機能化学　I
水曜3限（6/9～7/21）
担当：　北條　博彦

7/21本日は質問コーナーです（出席はとりません）

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