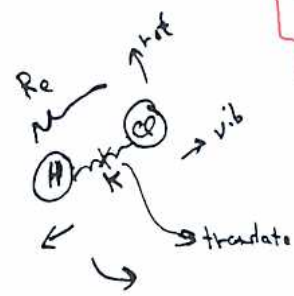


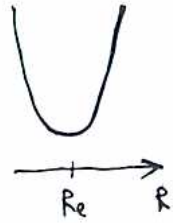
Chem. 1480
2/2/07

Gaseous
Diatomics Heteronuclear, 1st



molecular $\epsilon_j = \epsilon_j^{\text{rot}} + \epsilon_j^{\text{vib}} + \epsilon_j^{\text{trans}} + \epsilon_j^{\text{elect}} + \cancel{\epsilon_j^{\text{nuc}}}$

Then $Q \approx q^N / N!$, $w = q^{\text{rot}} q^{\text{vib}} q^{\text{trans}} q^{\text{elect}} q^{\text{nuc}}$
 $m \rightarrow M = m_H + m_{Cl}$ in Monatomic result

q^{vib} : 
 $v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$; $\mu = \frac{m_H m_{Cl}}{M}$; $q^{\text{vib}} = \frac{1}{2 \sinh(\beta h \nu / 2)}$
force constant of spring

q^{rot} :
 $(*) \quad q^{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-BJ(J+1)/kT}$; $B = \frac{h^2}{2\mu R_e^2}$ [Rotational Constant]

[Low T; sum explicitly]
 At high T [Rm. T for HCl], approximate $\sum \rightarrow \int du$ $u = J(J+1)$
 $du = (2J+1) dJ$

so $q^{\text{rot}} \approx \int_0^{\infty} du e^{-Bpu} = \frac{1}{\beta B} = \frac{kT}{B} = \frac{2kT \mu R_e^2}{h^2} = \frac{2kT I}{h^2} = \frac{8\pi^2 kT I}{h^2}$
 heteronuclear = T/σ

homonuclear, high T
 Heteronuclear diatomic: At high T, $q^{\text{rot}} = \frac{1}{\sigma} \cdot \frac{8\pi^2 kT I}{h^2}$, $\sigma = 2$ = "symmetry #" [classical] $\{2 \rightarrow 8$ indistinguishability

WARNING: At low T, $q^{\text{rot}} \neq (*)$, due to additional quantum mechanical restrictions [e.g. nuc. stat \neq nuc. rot]
 or wt's [symmetric or anti-symm. wrt to nuclear exchange] \rightarrow "ortho, para" H_2 ...

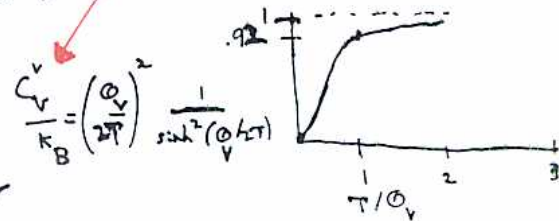
Internal E's, heat capacities [assume high T q^{rot}] : $\bar{E} = -\frac{1}{\beta} \ln \left[q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} \frac{1}{N!} \right]$
 no β dependence

(2)

$$\delta \bar{E} = \bar{E}_{\text{trans}} + \bar{E}_{\text{vib}} + \bar{E}_{\text{rot}} = \frac{3}{2} k_B T + \frac{h\nu}{2} \coth\left(\frac{\beta h\nu}{2}\right) + k_B T$$

[constant volume] heat capacity of one harmonic oscillator
 $\Theta_v = h\nu/k$

Compute $\bar{E}_{\text{rot}} = \frac{-1}{\Omega} \left[\frac{1}{\Omega} \right] = \frac{1}{\beta} = k_B T$ ✓ classical, equipartition [indep. of σ]



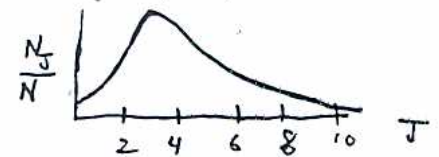
and $\frac{C_{v,m}}{R} = \frac{C_v}{N_A k_B} = \frac{3}{2} + \frac{\left[\frac{h\nu}{2}\right]^2}{\sinh^2(\beta h\nu/2)} + 1$

High T $\rightarrow \frac{5}{2}$ ✓
 Low T $\rightarrow \frac{3}{2}$ ✓

[assume $T \gg \beta/k_B$]

Aside on rotational populations $\frac{N_J}{N} = \frac{(2J+1)e^{-\beta B J(J+1)}}{\delta_{\text{rot}}}$

← typically some excited state population at rm. T.



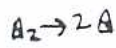
Avogadro's #

Aside on ideal gas Eqn. of state; for both monatomic, diatomic [also polyatomic]

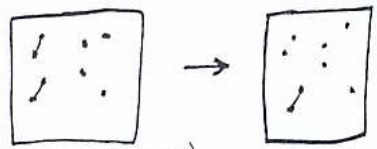
ideal gases,

$$\delta = \frac{f(T)V}{\text{essential structure}}, \text{ so } P = \frac{-JA}{JV} = +k_B T \frac{1}{JV} N \ln g = +Nk_B T \frac{\frac{1}{f(T)V} [f(T)V]}{f(T)V}$$

$$= +\frac{Nk_B T}{V} = \frac{\gamma RT}{V}$$



Chemical Equilibrium



$\Delta n_{A_2} = -1$ } Stoichiometric
 $\Delta n_B = 2$ } constraint.

Thus

$\Delta G = 2\mu_B - \mu_{A_2}$; at equilibrium $\Delta G = 0$
 $= \mu_B \Delta n_B + \mu_{A_2} \Delta n_{A_2}$

← general relationship for chemical equilibrium

Apply stat. mech; Boltz. stats: $A_B = -kT \ln Q_B$; $Q_B = \frac{g_B^{N_B} / N_B!}{g_{B_2}^{N_{B_2}} / N_{B_2}!}$; g_B = "molecular" pf ; also for B_2 .
 N_B = # B atoms

$\mu_B = \left(\frac{\partial A_B}{\partial N_B} \right)_{V,T} = -kT \frac{\partial}{\partial N_B} [N_B \ln g_B - \ln N_B!]$
 $= -kT \left\{ \ln g_B - \ln N_B \right\}$

Then,

Equilib. condit: $2\mu_B - \mu_{B_2} = 0 \Rightarrow 0 = 2[\ln g_B - \ln N_B] - [\ln g_{B_2} - \ln N_{B_2}]$

or $\frac{N_B^2}{N_{B_2}} = \frac{g_B^2}{g_{B_2}}$ or $\frac{[B]^2}{[B_2]} = \frac{(g_B/V)^2}{(g_{B_2}/V)} = K_c(T)$

N_B : volume eliminated if ideal gas.

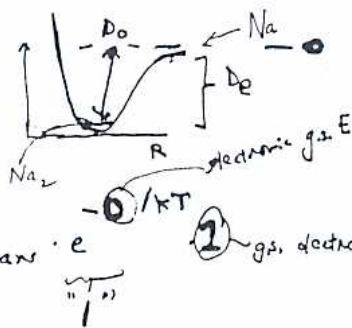
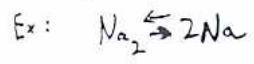
$[B] = N_B/V$
 = # density
 [molecular!]

Generalization: $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$ (general ideal gas rxn.)

Equilibrium: $[\nu_C \mu_C + \nu_D \mu_D] - [\nu_A \mu_A + \nu_B \mu_B] = 0$
 (Therm.) \Rightarrow Stat. mech Boltz. stats.

$\frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}} = \frac{(g_C/V)^{\nu_C} (g_D/V)^{\nu_D}}{(g_A/V)^{\nu_A} (g_B/V)^{\nu_B}} = K_c(T)$

Atkins



Example 20-11 Evaluating an equilibrium constant

Evaluate the equilibrium constant for the dissociation $Na_2(g) = 2Na(g)$ at 1000 K from the following data: $B = 0.1547 \text{ cm}^{-1}$, $\tilde{\nu} = 159.2 \text{ cm}^{-1}$, $D_0 = 70.4 \text{ kJ mol}^{-1}$ (0.73 eV). The Na atoms have doublet ground term.

(*) Ex. 17.6 in Atkins, Ed. 8.

$g_{Na} = g_{trans} \cdot e$
 2 g_{Na} = electronic degeneracy [Sodium doublet]

(4)

$+De/kT$ [\leftarrow electronic degeneracy = 1]

$q_{No_2} = \text{trans} \cdot \text{vib} \cdot \text{rot} \cdot \frac{q_e}{kT}$

Hence

$$K_c(T) = \left\{ \left[\frac{2\pi m_{No_2} kT}{h^2} \right]^{3/2} \cdot 2 \right\}^2$$

$$\left[\frac{2\pi m_{No_2} kT}{h^2} \right]^{3/2} \left[\frac{1}{2} \cdot \frac{8\pi^2 I kT}{h^2} \right] \left[\frac{1}{2 \cdot \sinh(h\nu/2kT)} \right] \left[\frac{De/kT}{e} \right]$$

\uparrow Homonuclear $\rightarrow \sigma^{-1}$ $\frac{kT}{h\nu} \text{ as } T \rightarrow \infty$

Note dep. at high T: $K(T) \propto \frac{T^3}{T^{3/2} T^2} = T^{-1/2}$

Note conversion to pressure; $\frac{N}{V} = \frac{P}{kT}$; thus $\frac{(P_c/kT)^{\nu_c} (P_D/kT)^{\nu_D}}{(P_A/kT)^{\nu_A} (P_B/kT)^{\nu_B}} = K_c(T)$

so $K_p(T) = \frac{P_c^{\nu_c} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} = (kT)^{\nu_c + \nu_D - \nu_A - \nu_B} K_c(T)$ (*) transformation to dimensionless form [as used in thermo]

hence in current example $K_p(T) = (kT) K_c(T) \sim T^{1/2}$ \leftarrow high T favors monomer [careful: not this simple because at ultra-high T's, excited electronic states enter.]

(*) $\Rightarrow \frac{(P_c/P^\ominus)^{\nu_c} (P_D/P^\ominus)^{\nu_D}}{(P_A/P^\ominus)^{\nu_A} (P_B/P^\ominus)^{\nu_B}} = \left(\frac{kT}{P^\ominus} \right)^{\nu_c + \nu_D - \nu_A - \nu_B} K_c(T) \equiv K_a(T)$ [dimensionless]

note $P_c/P^\ominus = a_c =$ "activity of C" for an ideal gas.

5

Na2 eq. mcd 141297 (Volts)

Calculation of equilibrium const for reaction Na2 --> 2 Na

In cgs units:

T = 1000 h = 6.626 · 10⁻²⁷ k = 1.38 · 10⁻¹⁶ mna = $\frac{23}{6.02 \cdot 10^{23}}$ mna2 = 2 · mna

The following Energies are in cm⁻¹:

B = 0.1547 nutw = 159.2 D0 = 70.4 · $\left(\frac{350}{4.184}\right)$ De = D0 + .5 · nutw kT = k · T · 5.03 · 10¹⁵

lamna = $\sqrt{\frac{h^2}{2 \cdot \pi \cdot mna \cdot k \cdot T}}$ lamna2 = $\sqrt{\frac{h^2}{2 \cdot \pi \cdot mna2 \cdot k \cdot T}}$

qrot = $\frac{kT}{B} \cdot \frac{1}{2}$ qvib = $\frac{1}{2 \cdot \sinh\left(\frac{nutw}{2 \cdot kT}\right)}$

[Note symmetry number factor of 1/2 in rot pf; also x2 in pf for Na due to electronic degeneracy]

Kc in units of cm⁻³:

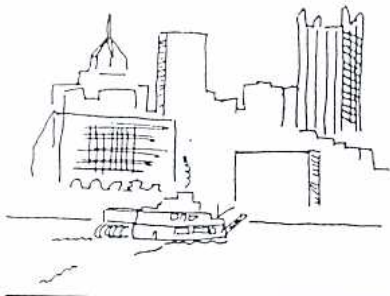
Kc = $\frac{\left(\frac{2}{lamna^3}\right)^2}{\left(\frac{1}{lamna2^3}\right) \cdot qrot \cdot qvib \cdot e^{\frac{De}{kT}}}$ Kc = 1.751 · 10¹⁹ Kp = Kc · k · T · $\left(\frac{1}{1.01 \cdot 10^6}\right)$ Kp = 2.392

Note conversion: 1 atm = 1.01 x 10⁶ dynes/cm²

Selected results for Kp:

Table with 2 columns: Temp and Keq. Rows: Temp0 = 1000 Keq0 = 2.39; Temp1 = 1500 Keq1 = 51.4; Temp2 = 2500 Keq2 = 657

Handwritten derivation of Kp = Kc · (kT/p°) and unit analysis. Shows Kc = (N_Na/kT)^2 / (N_Na2/v) = (P_Na/kT)^2 / (P_Na2/kT) = (P_Na/p°)^2 / (P_Na2/p°) · P/p°. Includes unit analysis: Kp = Kc · (kT/p°) with units cm⁻³ and cm³ units.



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ON RAMAN SPECTROSCOPY

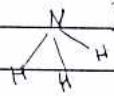
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Organizing Committee:
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S. A. Asher (Chair)
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P. W. Jagodzinski
F. A. Miller
L. A. Peteanu
P. B. Stein
G. C. Walker



Polyatomic Ideal Gases:

for linear molecules [e.g. $O=C=O$]: $3N-5$ vibr, 2 rotr
for nonlinear molecule [e.g. N]: $3N-6$ vibr, 3 rotr

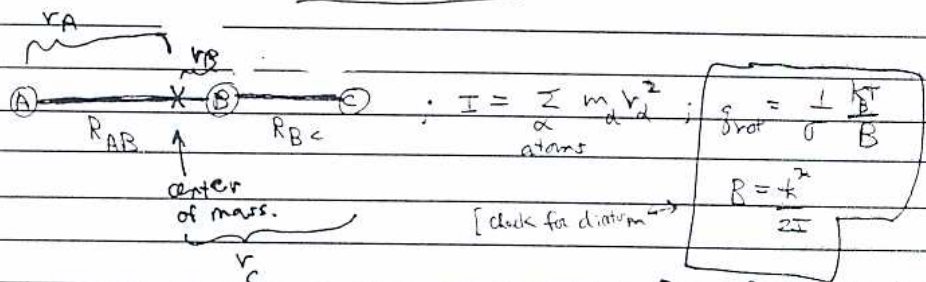


Energies:

Assuming nearly rigid molecule, $E_{\text{rotr}} = \text{rigid top energy} + \sum_k \text{h.o. vib } E(\omega_k)$
normal modes

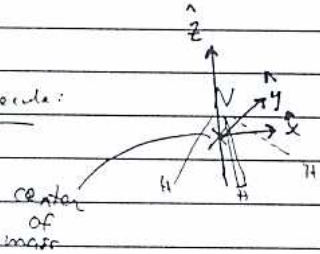
Rotational states, energy levels depend on (principal) moments of inertia

Linear molecule:



[check for diatom ->]
 $\sigma = 2$ for $A-B-A$, etc.;
otherwise $\sigma = 1$

Non-linear molecule:



Symmetry axes = Principal Axes of Rotation

(NB: \exists systematic procedure for locating $\hat{x}, \hat{y}, \hat{z}$ for systems w/ arbitrarily low symmetry)

$I_z = \sum_{\text{atoms}} m_d (x_d^2 + y_d^2)$; likewise for I_x, I_y

Then:

(4) $B_{\text{rot}} = \frac{1}{2} \frac{h^2}{\sigma} \left[\frac{h^2}{8 \pi^2 I_x} + \frac{h^2}{8 \pi^2 I_y} + \frac{h^2}{8 \pi^2 I_z} \right]$; $B_z = \frac{h^2}{8 \pi^2 I_z}$, etc.

symmetry # = # proper rotations in the symmetry group [$\sigma = 2$, H_2O
[Atkins, Chapt. 15] $\sigma = 3$, NH_3
 $\sigma = 12$, CH_4]



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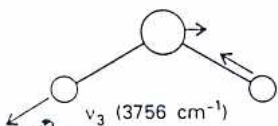
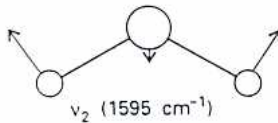
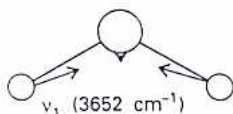


(nearly rigid)
vibrations: in polyatomic molecules, \exists $3N-6$ / $3N-5$ (for nonlinear/linear molecules)
distinct patterns of vibration, each characterized by sinusoidal variation of displacement of every atom from its equilibrium position. Thus each "normal mode" of vibration is characterized by a particular frequency.
[Detail of the mode amplitudes & vibrational frequencies depends on restoring forces experienced upon distortion from equilibrium.]

Ex:

580

(A+KIR)



Ed

16.48 The three normal modes of H_2O . The mode ν_2 is predominantly bending, and occurs at lower wavenumber than the other two.

[Fig. 13.41, Ed. 8]

Partition fn:

$$q_{\text{vib}} = \prod_k \frac{1}{Z \sinh(\beta h \nu_k / 2)}$$

(normal modes of vibration) frequency of kth normal mode

The heat capacity of a polyatomic molecule

for linear-molecule

$$C_{v,m} = \frac{3}{2}R + R + \sum_{k=1}^{3N-5} R f(y_k)$$

translation of c.m. rotation [follows eq. (4)]

$$f(y) = \frac{y^2}{\sinh^2 y} \quad \text{and} \quad y_k = \frac{\beta h \nu_k}{2}$$

detail of mode k.

High and Low T limits w.r.t. vibrations:

high T $\Rightarrow f \rightarrow 1 \Rightarrow C_{v,m} = \frac{5}{2}R + (3N-5)R$

low T $\Rightarrow f \rightarrow 0 \Rightarrow C_{v,m} = \frac{5}{2}R$

for non-linear polyatomic: $C_{v,m} = \frac{3}{2}R + \frac{3}{2}R + \sum_{k=1}^{3N-6} R f(y_k)$

high T $\Rightarrow C_{v,m} = 3R + (3N-6)R$

low T $\Rightarrow C_{v,m} = 3R$

vibrations "frozen out"