Experimental methods in trace gas research

04-04-2012

Please use the provided paper sheets to write down the solutions of the problems. Write your name and student ID number on a first page and enumerate all subsequent pages. Do not forget to hand in your paperwork after the examination.

Problem 1.

a) Show that a dipole momentum of the system of charged particles is independent upon choice of the reference frame if the system's total charge is zero.

b) Make a sketch of OH molecule and show direction of its dipole momentum.

c) Eigen wavefunctions $\Psi_n(x)$ of one-dimensional harmonic oscillator have the following properties:

$$\int_{-\infty}^{\infty} \Psi_n(x)\Psi_m(x)dx = \delta_{mn}$$

where $\delta_{mn} = 1$ if $m=n$ and $\delta_{mn} = 0$ if $m \neq n$

$$\Psi_{n+1}(x) = \sqrt{\frac{2}{n+1}} x\Psi_n(x) + \sqrt{\frac{n}{n+1}} \Psi_{n-1}$$

Find selection rules for a dipole transition in the one-dimensional harmonic oscillator.

Problem 2.

In first approximation, hydrogen cyanide HCN can be considered as a molecule of linear structure with a rotational constant $B = 1.4784\ cm^{-1}$.

a) How many vibrational degrees of freedom does this molecule have?
b) Is rotational constant of DCN molecule larger or smaller than that of HCN molecule? Explain your answer.
c) The wavenumber of the P(7) line in the vibrational band (020-000) of HCN molecule is 1379.8839 cm^{-1}. Find position of the P(8) line at the same band of this molecule.

Problem 3.

A researcher is going to build a LIF setup for measuring distribution of concentrations of sodium atoms during plasma deposition process. The pressure is sufficient low that collisional depopulation of the excited level can be neglected.

a) The researcher has a tunable laser with power 100 mW and linewidth 10^8Hz. Is het possible to reach saturation for the transition with wavelength of 589 nm utilizing the laser beam with cross-section of 1 mm^2? In estimations, the sodium atom can be considered as a two-level system and the degeneracies of the upper and lower levels can be put equal to 1.
b) The temperature of the buffer gas in the setup increased 4 times. How many times should pressure be changed to hold the rate of collisional depopulation constant?
c) The researcher estimated that the fluorescence signal is collected from the probe volume of cylindrical form with size of $100mm^2x5mm$ in the solid angle 10^{-3}sr. Quantum efficiency of a photodetector is 0.1 and transmittance of a collecting lens is 0.9. Assuming full saturation and Poisson statistics for collected photoelectrons, calculate the sampling time needed to measure the signal with 10% uncertainty when concentration of sodium atoms is $10^8 cm^{-3}$. The Einstein coefficient A_{ik} for this transition is $0.6 \cdot 10^8$ s^{-1}

Problem 4.

a)

i. Name and explain three different approaches to derive greenhouse gas fluxes, actually making use of concentration measurements.
ii. Describe the working (incl. the kind of input data) of bottom-up and top-down greenhouse gas concentration models. Are the models independent of each other? What can you say about greenhouse gas concentration forecasts with both model types? Give reasons for your answers.
iii. Explain how the Radon ingrowth method can be applied to verify the national methane emissions, e.g. of the Netherlands. Which input data are needed, how well are they known?

b)

i. Which properties are used in gas chromatography for qualitative, respectively quantitative analysis of an unknown mixture?
ii. Using a given gas chromatographic system, what can you do to enhance the separation of different compounds?
iii. Describe the basic working principles of a flame ionization detector (FID).

c)

i. Describe what happens if the pressure in the bellows of a dual-inlet IRMS system becomes too low (i.e., lower than approximately 10 mbar for CO_2)?
ii. Name three different types of mass spectrometric analyzers.
iii. Explain how a N_2O-concentration measurement can be done by mass spectrometry on an atmospheric CO_2/N_2O-sample. Explain what the result is used for.

Physical constants and conversion factors

Velocity of light in vacuum	c	$2.99792458 \cdot 10^{10}$ cm/s
Planck's constant	h	$6.626076 \cdot 10^{-27}$ erg·s
Electronic charge	e	$4.803206 \cdot 10^{-10}$ abs.e.s.u.
Electronic mass	m_e	$9.109390 \cdot 10^{-28}$ g
Mass of proton	m_p	$1.672623 \cdot 10^{-24}$ g
1/12 mass of the C^{12} atom	M_1	$1.660540 \cdot 10^{-24}$ g
Number of atoms in mole	N_A	$6.022137 \cdot 10^{23}$
Boltzamann's constant	k	$1.38066 \cdot 10^{-16}$ erg/K
Gas constant per mole	R	$8.31451 \cdot 10^{7}$ erg/K·mole

Conversion factors for energy units

	1 J	**1 erg**	**1 eV**	**1 K**	**1 cm^{-1}**
1 J	1	10^{7}	$6.2415 \cdot 10^{18}$	$7.2429 \cdot 10^{22}$	$5.0341 \cdot 10^{22}$
1 erg	10^{-7}	1	$6.2415 \cdot 10^{11}$	$7.2429 \cdot 10^{15}$	$5.0341 \cdot 10^{15}$
1 eV	$1.6022 \cdot 10^{-19}$	$1.6022 \cdot 10^{-12}$	1	11604	8065.5
1 K	$1.3807 \cdot 10^{-23}$	$1.3807 \cdot 10^{-16}$	$8.6174 \cdot 10^{-5}$	1	0.69504
1 cm^{-1}	$1.9864 \cdot 10^{-23}$	$1.9864 \cdot 10^{-16}$	$1.2398 \cdot 10^{-4}$	1.4388	1

Standard Atomic Weights.

Period \ Group	I	II	III	IV	V	VI	VII	VIII		
1	1520 $_{1}$H 1.0079 Hydrogen	0.008 $_{2}$He 4.003 Helium								
2	20 Li 6.941 Lithium	2.6 $_{4}$Be 9.012 Berillium	10 $_{5}$B 10.81 Boron	480 $_{6}$C 12.011 Carbon	25 $_{7}$N 14.007 Nitrogen	474000 $_{8}$O 15.999 Oxygen	950 $_{9}$F 18.998 Fluorine	$7 \cdot 10^{-5}$ $_{10}$Ne 20.180 Neon		
3	23000 $_{11}$Na 22.990 Sodium	23000 $_{12}$Mg 24.305 Magnesium	82000 $_{13}$Al 26.982 Aluminium	277000 $_{14}$Si 28.086 Silicon	1000 $_{15}$P 30.974 Phosphorus	260 $_{16}$S 32.065 Sulfur	130 $_{17}$Cl 35.453 Chlorine	1.2 $_{18}$Ar 39.948 Argon		
4	21000 $_{19}$K 39.098 Potassium	41000 $_{20}$Ca 40.08 Calsium	16 $_{21}$Sc 44.956 Scandium	5600 $_{22}$Ti 47.867 Titanium	160 $_{23}$V 50.942 Vanadium	100 $_{24}$Cr 51.996 Chromium	950 $_{25}$Mn 54.938 Manganese	41000 $_{26}$Fe 55.845 Iron	20 $_{27}$Co 58.933 Cobalt	80 $_{28}$Ni 58.69 Nickel
	50 $_{29}$Cu 63.546 Copper	75 $_{30}$Zn 65.409 Zinc	18 $_{31}$Ga 69.723 Gallium	1.8 $_{32}$Ge 72.64 Germanium	1.5 $_{33}$As 74.922 Arsenic	0.05 $_{34}$Se 78.96 Selenium	0.37 $_{35}$Br 79.904 Bromine	$1 \cdot 10^{-5}$ $_{36}$Kr 83.798 Krypton		
5	90 $_{37}$Rb 85.468 Rubidium	370 $_{38}$Sr 87.62 Strontium	30 $_{39}$Y 88.906 Yttrium	190 $_{40}$Zr 91.224 Zirconium	20 $_{41}$Nb 92.906 Niobium	1.5 $_{42}$Mo 95.94 Molibdenum	$7 \cdot 10^{-4}$ $_{43}$Tc [97.907] Technetium	0.001 $_{44}$Ru 101.07 Ruthenium	$2 \cdot 10^{-4}$ $_{45}$Rh 102.91 Rhodium	$6 \cdot 10^{-4}$ $_{46}$Pd 106.42 Palladium
	0.07 $_{47}$Ag 107.87 Silver	0.11 $_{48}$Cd 112.41 Cadmium	0.049 $_{49}$In 114.82 Indium	2.2 $_{50}$Sn 118.70 Tin	0.2 $_{51}$Sb 121.76 Antimony	0.005 $_{52}$Te 127.60 Tellurium	0.14 $_{53}$I 126.90 Iodine	$2 \cdot 10^{-6}$ $_{54}$Xe 131.29 Xenon		
6	3.0 $_{55}$Cs 132.90 Cesium	500 $_{56}$Ba 137.33 Barium	32 $_{57}$La 138.90 Lanthanum	3.3 $_{72}$Hf 178.49 Hafnium	2.0 $_{73}$Ta 180.95 Tantalum	1.0 $_{74}$W 183.84 Tungsten	$4 \cdot 10^{-4}$ $_{75}$Re 186.21 Rhenium	$1 \cdot 10^{-4}$ $_{76}$Os 190.23 Osmium	$3 \cdot 10^{-6}$ $_{77}$Ir 192.22 Iridium	0.001 $_{78}$Pt 195.08 Platinum
	0.0011 $_{79}$Au 196.97 Gold	0.05 $_{80}$Hg 200.59 Mercury	0.6 $_{81}$Tl 204.38 Thallium	1.4 $_{82}$Pb 207.2 Lead	0.048 $_{83}$Bi 208.98 Bismuth	$_{84}$Po [208.98] Polonium	$_{85}$At [209.99] Astatine	$_{86}$Rn [222.02] Radon		
7	$_{87}$Fr [223.02] Francium	$6 \cdot 10^{-7}$ $_{88}$Ra [226.02] Radium	$_{89}$Ac [227.03] Actinium							

Abundance in Earth crust, 10^{-4} %

Symbol — $_{42}$Mo; Atomic number — 42; 1.5; 95.94; Molibdenum

Element Atomic weight

Lantanides

68 $_{58}$Ce 140.12 Cerium	9.5 $_{59}$Pr 140.91 Praseodymium	38 $_{60}$Nd 144.24 Neodymium	$_{61}$Pm [144.91] Promethium	7.9 $_{62}$Sm 150.36 Samarium	2.1 $_{63}$Eu 151.96 Europium	7.8 $_{64}$Gd 157.25 Gadolinium
1.1 $_{65}$Tb 158.92 Terbium	6.0 $_{66}$Dy 162.50 Dysprosium	1.4 $_{67}$Ho 164.93 Holmium	3.8 $_{68}$Er 167.26 Erbium	0.48 $_{69}$Tm 168.93 Thulium	5.3 $_{70}$Yb 173.04 Ytterbium	0.51 $_{71}$Lu 174.97 Lutetium

Actinides

12 $_{90}$Th 232.04 Thorium	$_{91}$Pa 231.04 Protactinium	2.4 $_{92}$U 238.03 Uranium	$_{93}$Np 237.05 Neptunium	$_{94}$Pu [244.06] Plutonium	$_{95}$Am [243.06] Americium		
$_{96}$Cm [247.06] Curium	$_{97}$Bk [247.07] Berkelium	$_{98}$Cf [251.08] Californium	$_{99}$Es [252.08] Einsteinium	$_{100}$Fm [257.10] Fermium	$_{101}$Md [258.10] Mendelevium		
$_{102}$No [259.10] Nobelium	$_{103}$Lr [262.11] Lawrencium	$_{104}$Rf [261.11] Rutherfordium	$_{105}$Db [262.11] Dubnium	$_{106}$Sg [266.12] Seaborgium	$_{107}$Bh [264.12] Bohrium	$_{108}$Hs [267] Hassium	$_{109}$Mt [268.14] Meitnerium

Formulas

$$\widehat{H}_t\Psi(\overrightarrow{R_1},\dots\overrightarrow{R_N},\overrightarrow{r_1},\dots,\overrightarrow{r_n}) = E\Psi(\overrightarrow{R_1},\dots\overrightarrow{R_N},\overrightarrow{r_1},\dots,\overrightarrow{r_n}) \quad (2.1)$$

$$\widehat{H}_t = -\frac{\hbar^2}{2}\sum_i^N\frac{\Delta_i}{M_i} - \frac{\hbar^2}{2}\sum_j^n\frac{\Delta_j}{m_e} + \sum_{i,j}\frac{Z_iZ_Je^2}{|\overrightarrow{R_i}-\overrightarrow{R_j}|} + \sum_{i,j}\frac{e^2}{|\overrightarrow{r_i}-\overrightarrow{r_j}|} - \sum_{i,j}\frac{Z_ie^2}{|\overrightarrow{R_i}-\overrightarrow{r_j}|} \quad (2.2)$$

$$\widehat{H}_e = -\frac{\hbar^2}{2}\sum_j^n\frac{\Delta_j}{m_e} + \sum_{i,j}\frac{e^2}{|\overrightarrow{r_i}-\overrightarrow{r_j}|} - \sum_{i,j}\frac{Z_ie^2}{|\overrightarrow{R_i}-\overrightarrow{r_j}|} + \sum_{i,j}\frac{Z_iZ_Je^2}{|\overrightarrow{R_i}-\overrightarrow{R_j}|}$$

$$\widehat{H}_N = -\frac{\hbar^2}{2}\sum_i^N\frac{\Delta_i}{M_i} \quad (2.3)$$

$$\widehat{H}_e\Psi_e(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) = E_e(\vec{R}_1,\dots,\vec{R}_N)\Psi_e(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) \quad (2.4)$$

$$\Psi(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) = \sum_k \Phi_n(\vec{R}_1,\dots,\vec{R}_N)\Psi_e^k(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) \quad (2.5)$$

$$\left(-\frac{\hbar^2}{2}\sum_i^N\frac{\Delta_i}{M_i} + E_e(R_1,\dots,R_N)\right)\Phi_k(\vec{R}_1,\dots,\vec{R}_N) = E\Phi_k(\vec{R}_1,\dots,\vec{R}_N) \quad (2.6)$$

$$E_e(R) = 4\epsilon\left(\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right) = \epsilon\left(\left(\frac{R_m}{R}\right)^{12} - 2\left(\frac{R_m}{R}\right)^6\right) \quad (2.7)$$

$$\widehat{H}_{rot}\Phi_r(q_r) = E_{rot}\Phi_r(q_r)$$

$$\widehat{H}_1\Phi_v(q_v) = E_1\Phi_v(q_v) \quad (2.7)$$

$$\mathrm{E_{rot}} = \frac{\hbar^2}{2\mathrm{I_M}}\mathrm{J(J+1)} = \mathrm{BJ(J+1)} \quad (2.10)$$

$$E_e(Q_1,\dots,Q_{N_{vib}}) \cong E_e(Q_1^0,Q_2^0,\dots,Q_{N_{vib}}^0) + \frac{1}{2}\sum_i\frac{\partial^2E_e}{\partial Q_i^2}(Q_i - Q_i^0)^2 \quad (2.11)$$

$$E_{vib} = \hbar\sum_i\omega_i\left(v_i + \frac{1}{2}\right) \quad (2.12)$$

$$E_{vib} = \hbar\sum_i\omega_i\left(v_i + \frac{1}{2}\right) - \hbar\sum_i\omega_ix_{ie}\left(v_i + \frac{1}{2}\right)^2 \quad (2.12)$$

$$E_{el}: E_{vib}: E_{rot} \sim 1: \sqrt{\frac{m_e}{M_N}} : \frac{m_e}{M_N} \quad (2.13)$$

$$E = E_{el}(R) + \hbar\omega_e\left(v + \frac{1}{2}\right) + B_{rot}J(J+1) \quad (2.14)$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi \quad (5.1)$$

$$\hbar\omega_0 = E_k - E_i \quad (5.2)$$

$$w_{ik} = \frac{2\pi}{3\hbar^2cg_k}(\vec{\mu}_{ik})^2\rho_\omega \quad (5.3)$$

$$\boxed{w_{ik} = B_{ik}\rho_\omega} \tag{5.4}$$

$$\boxed{w_{ki} = A_{ki} + B_{ki}\rho_\omega} \tag{5.5}$$

$$\boxed{A_{ki} = \frac{2\hbar\omega^3}{\pi c^3} B_{ki} \ \ and\ B_{ki} = B_{ik}\frac{g_i}{g_k}} \tag{5.6}$$

$$\boxed{I_\omega = N_\omega c \quad \left[\frac{photons}{m^2 s}\right]} \tag{5.7}$$

$$\boxed{I = \hbar\omega N_\omega c \ \left[\frac{W}{m^2}\right]} \tag{5.8}$$

$$\boxed{\nu = \frac{c}{\lambda}} \tag{5.9}$$

$$\boxed{\tilde{\nu} = \frac{1}{\lambda} = \frac{c}{\nu}} \tag{5.10}$$

$$\boxed{\sigma_{ik} = \frac{B_{ik}}{c}\hbar\omega_{ki}} \tag{5.11}$$

$$\boxed{I_\omega(x) = I_\omega(0)\, exp(-\sigma_{ik}N_i x)} \tag{5.12}$$

$$\boxed{I_\omega(x) = I_\omega(0) exp(-k_{ik}x)} \tag{5.13}$$

$$\boxed{N_i = N\frac{g_i\, exp\left(-\frac{E_i}{kT}\right)}{Z(T)}} \tag{5.14}$$

$$\boxed{Z(T) = \sum_i g_i\, exp\left(-\frac{E_i}{kT}\right)} \tag{5.15}$$

$$\boxed{Z(T) = Z_{rot}(T) \cdot Z_{vib}(T) \cdot Z_{el}(T)} \tag{5.16}$$

$$\boxed{Z_{rot}(T) = \sum_j (2j+1)e^{-\frac{Bj(j+1)}{kT}} \cong \int 2xe^{-Bx^2}dx = \frac{kT}{B}} \tag{5.17}$$

$$\boxed{N_{vJ} = N_v(2j+1)\frac{B}{kT}exp\left(-\frac{Bj(j+1)}{kT}\right)} \tag{5.18}$$

$$\boxed{Z_{vib}(T) = \sum_n e^{-\frac{\hbar\omega_{vib}n}{kT}} = \frac{1}{1-exp\left(-\frac{\hbar\omega}{kT}\right)}} \tag{5.19}$$

$$\boxed{N_v = N_e\, exp\left(-\frac{\hbar\omega_{vib}n}{kT}\right)\left(1 - exp\left(-\frac{\hbar\omega_{vib}}{kT}\right)\right)} \tag{5.20}$$

$$\boxed{k_{ik}(\omega) = K_{ik}L_\omega(\omega)} \tag{5.21}$$

$$\boxed{I_\omega(\omega) = \frac{2\pi}{\lambda^2}I_\lambda(\lambda) = 2\pi c I_{\tilde{\nu}}(\tilde{\nu})} \tag{5.22}$$

$$\boxed{L(\omega) \ = \frac{2\Delta\omega_n}{\pi}\frac{1}{4(\omega-\omega_{ki})^2+\Delta{\omega_n}^2}} \tag{5.23}$$

$$\Delta\omega_n = \frac{1}{\tau_k} = \sum_i A_{ki} \tag{5.24}$$

$$L(\omega) = \frac{2}{\Delta\omega_D}\sqrt{\frac{\ln 2}{\pi}}\, exp\left(-4\ln 2\left(\frac{\omega-\omega_0}{\Delta\omega_D}\right)^2\right) \tag{5.25}$$

$$\Delta\omega_D = 2\frac{\omega_0}{c}\sqrt{\frac{(2\ln 2)RT}{M}} \tag{5.26}$$

$$L(\omega) = \int_{-\infty}^{\infty} L_L(\omega')L_D(\omega-\omega')\,d\omega' = \frac{4\Delta\omega_L}{\pi\Delta\omega_D}\sqrt{\frac{\ln 2}{\pi}}\int_{-\infty}^{\infty}\frac{1}{4(\omega'-\omega-\omega_0)^2+\Delta\omega_L{}^2}\, exp\left(-4\ln 2\left(\frac{\omega'-\omega_0}{\Delta\omega_D}\right)^2\right)d\omega' \tag{5.27}$$

$$\hbar\omega = E' - E'' = E'_e + E'_{vib} + E'_{rot} - E''_e - E''_{vib} - E''_{rot} \tag{6.1}$$

$$\tilde{\nu} = E'_{rot} - E''_{rot} = BJ'(J'+1) - BJ''(J''+1) \tag{6.2}$$

$$\tilde{\nu} = B(J+1)(J+2) - BJ\,(J+1) = 2B(J+1) \tag{6.3}$$

$$\tilde{\nu} = E'_{vib} + E'_{rot} - E''_{vib} - E''_{rot} = \tilde{\nu}_0\left(v'+\frac{1}{2}\right) + BJ'(J'+1) - \tilde{\nu}_0\left(v''+\frac{1}{2}\right) - BJ''(J''+1) \tag{6.4}$$

$$\tilde{\nu}_P = \tilde{\nu}_0 + B(J-1)J - BJ(J+1) = \tilde{\nu}_0 - 2BJ \tag{6.5}$$

$$\tilde{\nu}_R = \tilde{\nu}_0 + B(J+1)(J+2) - BJ\,(J+1) = \tilde{\nu}_0 + 2B + 2BJ \tag{6.6}$$

$$S_{ik} = \frac{h\tilde{\nu}}{c}\frac{N_i}{N}\left(1-\frac{g_i}{g_k}\frac{N_k}{N_i}\right)B_{ik} \tag{6.7}$$

$$S_{ik}(T) = S_{ik}(T_{ref})\frac{Z(T_{ref})}{Z(T)}\frac{exp\left(-\frac{c_2E_i}{T}\right)}{exp\left(-\frac{c_2E_i}{T_{ref}}\right)}\frac{\left(1-exp\left(-\frac{c_2\tilde{\nu}_{ik}}{T}\right)\right)}{\left(1-exp\left(-\frac{c_2\tilde{\nu}_{ik}}{T_{ref}}\right)\right)} \tag{6.8}$$

$$k_{ik}(\tilde{\nu},P,T) = S_{ik}(T)L_{\tilde{\nu}}(\tilde{\nu},P,T)N \tag{6.9}$$

$$k(\tilde{\nu},P,T) = \sum_j S_j(T)L_{j,\tilde{\nu}}(\tilde{\nu},P,T)\frac{X_jP}{kT} \tag{6.10}$$

$$\Delta\tilde{\nu}_L = \left(\frac{T_{ref}}{T}\right)^n\left(\gamma_{air}(1-X_j) + \gamma_{self}X_j\right)P \tag{6.11}$$

$$N = \frac{1}{S_{ik}(T)L_{\tilde{\nu}}(\tilde{\nu},P,T)l}\ln\left(C\frac{I_2}{I_1}\right) \tag{6.12}$$

$$N = \frac{\delta\tilde{\nu}}{S_{ik}(T)l}\sum_i \ln\left(C\frac{I_2(\tilde{\nu}_i)}{I_1(\tilde{\nu}_i)}\right) \tag{6.13}$$

$$\boxed{N = AS + B} \tag{6.14}$$

$$\boxed{N_{lim} = \frac{1}{S_{ik}L_\nu l}\sqrt{\left(\frac{\delta I_2}{I_2}\right)^2 + \left(\frac{\delta I_1}{I_1}\right)^2}} \tag{6.15}$$

$$\begin{aligned} \frac{dN_k}{dt} &= \frac{B_{ik}}{c} I_\nu N_i - \frac{B_{ki}}{c} I_\nu N_k - (A_{ki} + Q_{ki})N_k \\ \frac{dN_i}{dt} &= -\frac{B_{ik}}{c} I_\nu N_i + \frac{B_{ki}}{c} I_\nu N_k + (A_{ki} + Q_{ki})N_k \end{aligned} \tag{7.1}$$

$$\boxed{N_k(t) = \frac{B_{ik}}{c} I_\nu N_0 \tau \left(1 - e^{-\frac{t}{\tau}}\right)} \tag{7.2}$$

$$\boxed{N_k = \frac{B_{ik}}{c} I_\nu N_0 \tau = N_0 \frac{B_{ik}}{B_{ik}+B_{ki}} \frac{1}{1+\frac{I_\nu^{sat}}{I_\nu}} = N_0 \frac{g_k}{g_k+g_i} \frac{1}{1+\frac{I_\nu^{sat}}{I_\nu}}} \tag{7.3}$$

$$\boxed{I_\nu^{sat} = \frac{(A_{ki}+Q_{ki})c}{B_{ik}+B_{ki}}} \tag{7.4}$$

$$\begin{aligned} N_k &= \frac{\frac{N_0 B_{ik}}{c} I_\nu}{A_{ki}+Q_{ki}} = \frac{N_0 g_k}{g_k+g_i} \frac{I_\nu}{I_\nu^{sat}}, \quad && I_\nu \ll I_\nu^{sat} \\ N_k &= \frac{N_0 g_k}{g_k+g_i}, && I_\nu \gg I_\nu^{sat} \end{aligned} \tag{7.5}$$

$$\boxed{I_{fl} = A_{ik} N_k \Delta V \frac{\Omega}{4\pi}} \tag{7.6}$$

$$\boxed{I_{fl} = \eta \epsilon A_{ik} N_k l S \frac{\Omega}{4\pi}} \tag{7.7}$$

$$\boxed{I_{fl} = \eta\epsilon \frac{\Omega}{4\pi} lS \frac{A_{ki}}{A_{ki}+Q_{ki}} \frac{N_0 B_{ik}}{c} I_\nu = \eta\epsilon \frac{\Omega}{4\pi} lS \frac{I_\nu}{I_V^{sat}} \frac{N_0 g_k}{g_i+g_k} A_{ki}} \text{ (linear)} \tag{7.7}$$

$$\boxed{I_{fl} = \eta\epsilon \frac{\Omega}{4\pi} lS \frac{N_0 g_k}{g_i+g_k} A_{ki}} \text{ (saturation)} \tag{7.8}$$

$$\boxed{N_{lim}^{sat} = \frac{1}{\eta\epsilon \frac{\Omega}{4\pi} lS \frac{g_k}{g_k+g_i} A_{ki} \Delta t}} \tag{7.9}$$

$$\boxed{I_{\nu,free}^{sat} = \frac{A_{ki} c}{B_{ik}(1+g_i/g_k)} = \frac{8\pi hc}{\lambda^3} \frac{g_k}{g_i+g_k}} \tag{7.10}$$

$$\boxed{I_\nu^{sat} = I_{\nu,free}^{sat} \frac{Q_{ik}}{A_{ik}}} \tag{7.11}$$

$$\begin{aligned} \frac{dN_k}{dt} &= \frac{B_{ik}}{c} I_\nu N_i - \frac{B_{ki}}{c} I_\nu N_k + \textstyle\sum_{j\neq k} Q_{jk} N_j \\ &\quad - N_k \textstyle\sum_{j\neq k} (Q_{kj} + A_{kj}) - N_k W_k \end{aligned} \tag{7.12}$$

$$\boxed{\frac{dN_k}{dt} = \frac{\frac{B_{ik}}{c} I_\nu N_0 e^{-\frac{E_i}{kT}}}{Z(T)} - N_k(Q_k + A_k)} \tag{7.13}$$

$$\boxed{S_{fl} = \int_0^{t_s} I_{fl}(t)dt = \eta\epsilon A_{ki}\frac{\Omega}{4\pi} lS \int_0^{t_s} N_k(t)dt = \eta\epsilon A_{ki}\frac{\Omega}{4\pi} l \frac{\frac{B_{ik}}{c} N_0 e^{-\frac{E_i}{kT}} E_l}{Z(T)(Q_k + A_k)\Delta\nu_l}} \tag{7.14}$$

$$\boxed{N_0 = N_{cal}\frac{S_{fl}}{S_{fl}^{cal}}\frac{E_l^{cal}}{E_l}} \tag{7.15}$$

$$\boxed{N_0 = N_{cal}\frac{S_{fl}}{S_{fl}^{cal}}\frac{E_l^{cal}}{E_l} e^{-\frac{E_i}{k}\left(\frac{1}{T_{cal}}-\frac{1}{T}\right)} \frac{Z(T)}{Z(T_{cal})}\frac{Q_k + A_k}{Q_{k,cal} + A_k}} \tag{7.16}$$

$$\boxed{\rho = \rho_p V N} \tag{13.1}$$

$$\boxed{\phi = VN} \tag{13.2}$$

$$\boxed{dN = n_d(d_p, \vec{r}, t) d(d_p)} \tag{13.3}$$

$$\boxed{\int_0^\infty n_d(d_p, \vec{r}, t)\, d(d_p) = N} \tag{13.4}$$

$$\boxed{\overline{d_p} = \frac{1}{N}\int_0^\infty d_p n_d(d_p, \vec{r}, t)\, d(d_p)} \tag{13.5}$$

$$\boxed{A = \int_0^\infty \pi d_p^2 n_d(d_p, \vec{r}, t)\, d(d_p)} \tag{13.6}$$

$$\boxed{\phi = \int_0^\infty \pi \frac{d_p^3}{6} n_d(d_p, \vec{r}, t)\, d(d_p)} \tag{13.7}$$

$$\boxed{I = \frac{I_0 F(\theta, \phi, \lambda)}{\left(\frac{2\pi r}{\lambda}\right)^2}} \tag{13.8}$$

$$\boxed{\sigma_{sc} = \left(\frac{\lambda}{2\pi}\right)^2 \int_0^{2\pi}\int_0^{\pi} F(\theta, \phi, \lambda) \sin\theta\, d\theta\, d\phi} \tag{13.9}$$

$$\boxed{Q_{sc} = \frac{\sigma_{sc}}{s_g}} \tag{13.10}$$

$$\boxed{Q_{sc} = \frac{\int_0^{2\pi}\int_0^{\pi} F(\theta, \phi, \lambda) \sin\theta\, d\theta\, d\phi}{\left(\frac{2\pi}{\lambda}\right)^2 s_g}} \tag{13.11}$$

$$\boxed{Q_{ext} = Q_{sc} + Q_{abs}} \tag{13.12}$$

$$\boxed{\vec{p} = \alpha\vec{E}} \tag{13.13}$$

$$\boxed{I = (1 + cos^2\theta)\frac{k^4\alpha^2}{2r^2} I_0} \tag{13.14}$$

$$\boxed{\alpha = \frac{3}{4\pi}\frac{(m^2 - 1)}{m^2 + 2} V} \tag{13.15}$$

$$Q_{sc} = \frac{8}{3}x^4 \frac{m^2-1}{m^2+2} \tag{13.16}$$

$$\begin{gathered} m = n - in' \\ n^2 - n'^2 = \epsilon \\ nn' = \frac{\lambda\sigma}{c} \end{gathered} \tag{13.17}$$

$$\mathrm{Q_{sc}} = \frac{8}{3}\mathrm{x}^4 \mathrm{Re}\left(\frac{\mathrm{m}^2-1}{\mathrm{m}^2+2}\right) \tag{13.18}$$

$$Q_{abs} = -4xIm\left(\frac{m^2-1}{m^2+2}\right) \tag{13.19}$$

$$P_{sc} = \frac{\pi d_p^2}{4} Q_{sc} N_p \Delta V I_0 \tag{13.20}$$

$$P_{sc} = \int_0^\infty \frac{\pi d_p^2}{4} Q_{sc}(d_p) n_p(d_p)\, d(d_p)\, \Delta V \tag{13.21}$$

$$dI = -I\left[\int_0^\infty \frac{\pi d_p^2}{4} Q_{ext}(d_p) n_p(d_p)\, d(d_p)\right] dx \tag{13.22}$$

$$k(x) = \int_0^\infty \frac{\pi d_p^2}{4} Q_{ext}(d_p) n_p(d_p)\, d(d_p) \tag{13.23}$$

$$I = I(0)e^{-\kappa L} = I(0)e^{-L\int_0^\infty \frac{\pi d_p^2}{4} Q_{ext}(d_p) n_p(d_p)\, d(d_p)} \tag{13.24}$$

$$k = \int_{-\infty}^{\infty} \frac{d\kappa}{d\log d_p}\, d\log d_p \tag{13.25}$$

$$\frac{d\kappa}{d\log d_p} = \frac{3}{2}\frac{Q_{ext}}{d_p} n_p(d_p) \frac{dV}{d\log d_p} \tag{13.26}$$