

Part-B

Chem. 447

Exam Answers

4. For AE, energy can be introduced by any thermal (collisional) means usually by use of a flame or plasma device. For stimulated emission, energy also can be introduced by collisions in an electrically discharge, by electric current in a diode junction or by the absorption of radiation (optical pump). Spontaneous emission occurs naturally after an average time equal to the lifetime of the excited state. For upper state q and lower state p , spontaneous emission is described by the rate equation

$$dn_q/dt = -A_{qp}n_q$$

where n_q is the population (atoms/cm³) in upper state q , and A_{qp} is the transition probability (rate constant) for the reaction $q = p + h\nu$. Stimulated emission occurs when a photon (stimulating photon) causes an excited atom or molecule to give up a photon and transition to the lower energy state. After the transition, the two photons are in phase (coherent) and have the same polarization. For upper state q and lower state p , stimulated emission is described by the rate equation

$$dn_q/dt = -B_{qp}n_q\rho_\nu$$

where n_q is the population in upper state q , ρ_ν is the radiation density at the transition frequency ν and B_{qp} is the transition probability for the reaction $q + h\nu = p + 2h\nu$. Spontaneous emission is used for atomic emission spectroscopy often with a flame, ICP, glow discharge or other plasma devices as a radiation source. It is used for the qualitative and quantitative analysis of the elements. Stimulated emission is used with a resonator to amplify the radiation and produce lasing action. Lasers are used for fluorescence, and other spectroscopic methods of analysis.

5. Assuming that the plasma is in thermodynamic equilibrium, the Boltzmann equation can be used to obtain the relative population in the excited state as a function of the plasma temperature. Assuming that the partition function is nearly constant over this relatively small temperature range, the ratio of the excited-state population n_q to the total population n_t is given by

$$n_q/n_t = \exp(-E_q/kT)/Z$$

where E_q is the energy of the excited state, k is the Boltzmann constant, T is the absolute temperature and Z is the partition function. From the problem, $E_q/k = 5.00 \times 10^4$, and at 5000K,

$$n_q/n_t = \exp(-10.00)/Z = 4.54 \times 10^{-5}/Z$$

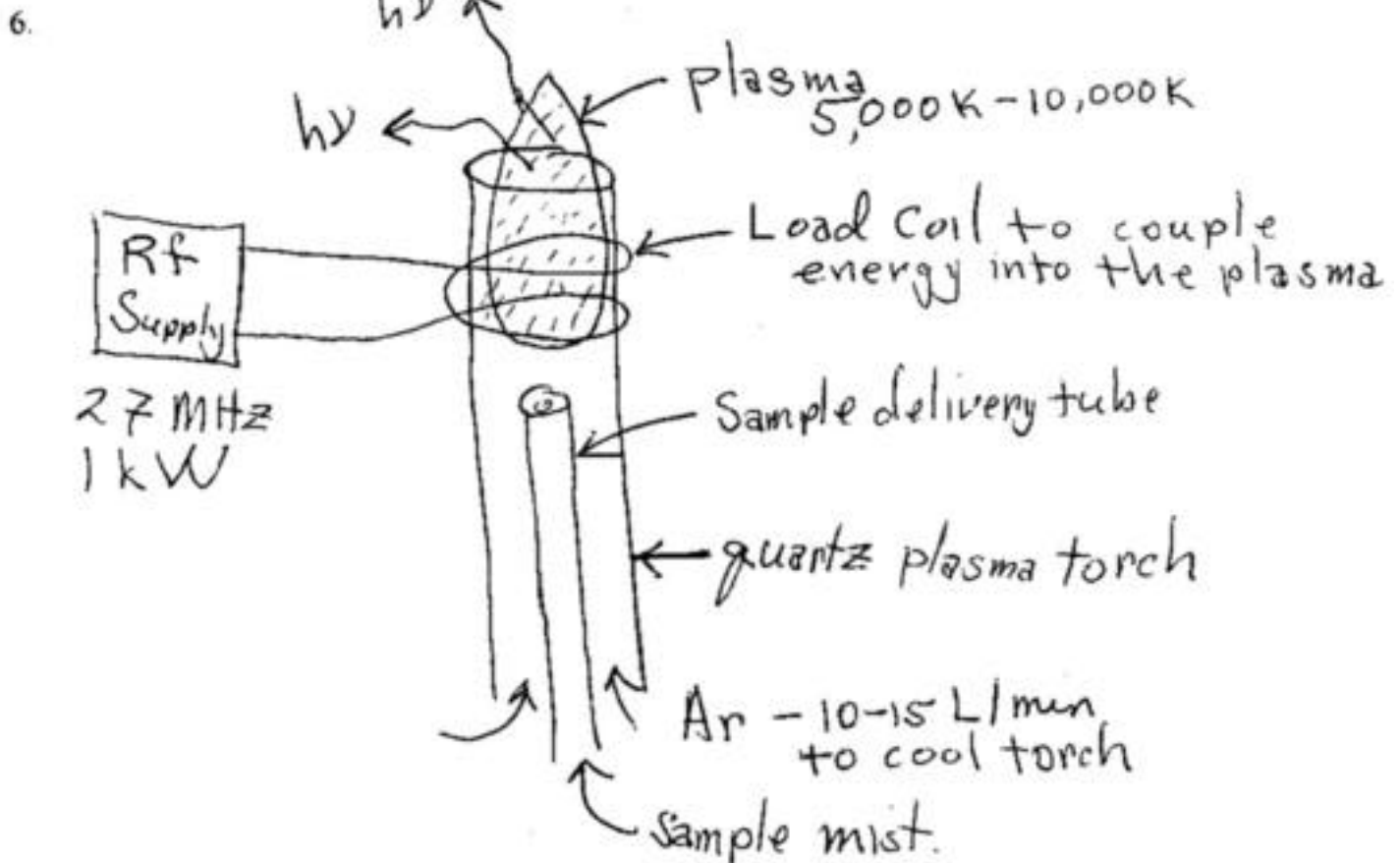
At 5100K,

$$n_q/n_t = \exp(-9.804)/Z = 5.52 \times 10^{-5}/Z$$

This gives an increase in intensity of

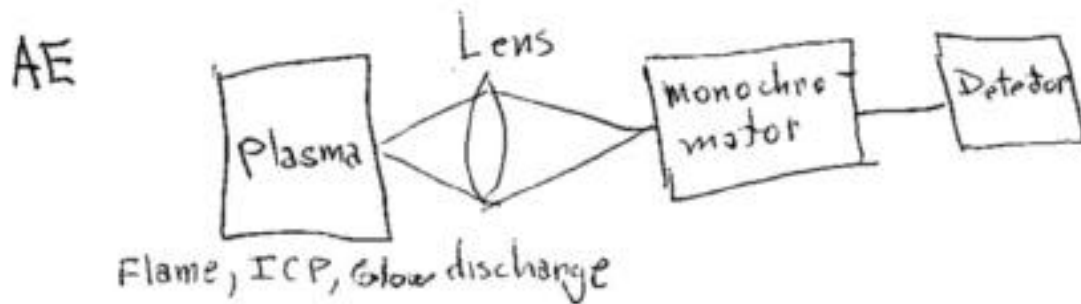
$$(5.52 \times 10^{-5} - 4.54 \times 10^{-5}) / 4.54 \times 10^{-5} = 0.216 = 21.6\%$$

This points out the need for very good control of plasma temperature. If the plasma was operated at lower pressure, collision frequency is reduced and the partitioning of energy coming into the plasma and leaving the plasma is slower. Thus, the plasma may not be in thermodynamic equilibrium and the Boltzmann equation does not work.



The rapidly changing axial magnetic field produced by the load coil causes electrons to move in circular paths around the magnetic field lines and absorb energy from the field. Collisions of these high-energy electrons with Ar atoms results in the production of Ar ions and more electrons. This sustains the plasma. Collisions of plasma electrons with sample atoms provides most of the energy for the population of excited state of the sample atoms. At 4 MHz, the plasma has a teardrop shape, and a thermal barrier of expanding gas prevents sample aerosol from penetrating the core of the plasma. At 27 MHz, the plasma shape changes, and a lower temperature core allows improved penetration of sample aerosol. This has been attributed to the skin effect at the higher frequency.

7. For atom emission, the sample atoms are heated by collisions in a flame or plasma resulting in the population of excited states. The radiative relaxation of these excited states produces the line spectra of the sample atoms. Radiation intensity at a specified wavelength is a linear function of the concentration of the sample atoms. For atomic absorption, ground-state atoms are produced in a flame or graphite furnace (sample cell). Radiation from a hollow-cathode lamp, using the target element as a cathode and producing the emission spectrum of the target element, is passed through the sample cell, and the intensity of an emission line from the target element is measured with a sample and with a blank. From these two intensity measurements, Beer's law is used to compute sample concentration from a calibration plot of absorbance vs. concentration.



With AE, it is straightforward to do simultaneous multi-element analyses. Detection limits for metallic elements in an ICP are much lower than for AA or AE in combustion flames, but instrument costs and operating costs (10-15 L/min. of Ar) are much greater with the ICP. For AA, the hollow cathode lamp must be changed for every element. Furnace AA is preferred for very small samples and can give very low absolute detection limits. Furnace AA is prone to interferences from the formation of small molecules, incomplete atomization and memory effects. Flame AA is very simple and can be very reproducible, since ground-state populations are much less effected by temperature than the excited state populations used for AE.