Possibly useful equations:

\[ \frac{N^*}{N_o} = \frac{g^*}{g_o} e^{-\frac{\Delta E}{kT}} \]
\[ \nu \lambda = c \]
\[ \Delta E = h \nu \]
\[ \Delta E = \frac{\gamma h}{2\pi} B_o \]

Boltzmann's constant \((k) = 1.381 \times 10^{-23} \text{ J K}^{-1}\)

Planck's constant \((h) = 6.626 \times 10^{-34} \text{ J s}^{-1}\)

Speed of light \((c) = 2.998 \times 10^8 \text{ m s}^{-1}\)

\[ \pi = 3.14159 \]

\[ R_{MS} = \frac{m}{\Delta m} \]

\[ k' = \frac{t_R - t_M}{t_M} \]

\[ \alpha = \frac{K_B}{K_A} \]

\[ R_{chromatography} = \frac{\Delta t_R}{w_{1/2} \text{ (average)}} \]

\[ N = 5.54 \left( \frac{t_R}{w_{1/2}} \right)^2 \]

\[ H = A + \frac{B}{u} + (C_S + C_M)u \]

\[ H = \frac{L}{N} \]

\[ u = \frac{L}{t_M} \]

\[ R_{chromatography} = \frac{1}{4} \sqrt{N} \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k_B}{1 + k_B} \right) \]

Please read the questions carefully and follow instructions. Be sure that your handwriting is clear, and indicate your answer. Use the correct units and a reasonable number of sig figs. If calculations are required, show your work in order to receive full or partial credit.

1. (4 pts) Choose the one correct answer. Which of the following ionization methods is most commonly used for atomic emission spectroscopy?

   a. flame
   b. graphite furnace
   c. plasma
   d. None of the above.

2. (4 pts) List the following atomic spectroscopy techniques in order from lowest to highest detection limits:

   Flame absorption
   Graphite furnace absorption
   Plasma emission
   Plasma mass spectroscopy

   lowest: plasma MS
   highest: flame
3. (8 pts) Consider the analysis of Magnesium using a graphite furnace operated at 2600K. What fraction of Mg atoms is in the excited state that has a $\Delta E$ corresponding to light at 589nm? The degeneracies of the excited and ground states are 2 and 1 respectively.

$$\Delta E = \frac{hc}{\lambda} \left( \frac{2.998 \times 10^8 \text{m/s}}{6.626 \times 10^{-34} \text{J s}} \right) = 3.37 \times 10^{-19} \text{ J}$$

$$\frac{N_x}{N_o} = 2e^{\frac{-3.37 \times 10^{-19}}{1.381 \times 10^{-23} \text{K} \cdot \text{J/K}} x 2600 \text{K}} = 1.67 \times 10^{-24}$$

4. (8 pts) The Heisenberg uncertainty principle determines the minimum line width for atomic energy transitions. Give one additional factor that broadens atomic absorption line widths. Explain why this occurs in 2 sentences or less.

- Pressure Broadening: collisions cause slight changes in $\Delta E$ and $t$ for individual $e^-$ transitions.
- Doppler Broadening: analyte moving towards or away from the detector causes an apparent shift in $\Delta E$ to shorter or longer $\lambda$.

5. (8 pts) List one advantage and disadvantage of soft ionization techniques used in mass spectroscopy.

- Advantage: Obtain molecular mass, less interferences, greater sensitivity
- Disadvantage: No definitive identification

6. (5 pts) For the following ionization techniques, indicate what phase (gas, liquid, or solid) the sample should be to use the technique. Only indicate one per method.

- Fast atom bombardment: solid
- Electron impact: gas
- Electrospray: liquid
- Matrix assisted laser desorption/ionization: solid, liquid
- Atmospheric pressure chemical ionization: gas, liquid

7. (8 pts) What resolving power does a mass analyzer need to separate two ions with mass to charge ratios of 88.0522 and 88.0345?

$$R = \frac{88}{0.0177} = 4972$$
8. (6 pts) Explain why all ion separation is done in a vacuum.

If separation was not carried out in a vacuum, ions would collide with other gas molecules, changing their trajectories causing a reduction in mass resolution, and the possibility of ions not reaching the detector at all.

9. (5 pts) Choose the one correct answer. Which of the following ion separation techniques has the highest possible resolution?

a. quadrupole
b. magnetic sector with electrostatic analyzer
c. ion trap
d. time of flight

10. (4 pts) NMR depends on radiation in the frequency.

a. UV
b. microwave
c. visible
d. radio

11. (10 pts) What is the magnetic field strength (T) of a 1.00 GHz NMR? The magnetogyric ratio for $^1$H is $2.6752 \times 10^8$ T$^{-1}$ s$^{-1}$.

\[
\Delta \nu = \frac{\gamma h}{2\pi} \quad B_0 = \frac{\nu Z \gamma (1.0 \times 10^7 \text{s}^{-1})}{2 \times 3.14159} \quad \frac{2.6752 \times 10^8 \text{T}^{-1} \text{s}^{-1}}{2.6752 \times 10^3 \text{T}^{-1} \text{s}^{-1}} \quad B_0 = [23.5 \text{T}]
\]

12. (4 pts) Choose the one correct answer. The coupling constant between two different types of protons on a 100 MHz NMR is 7.6 Hz. The coupling constant for these same two protons on a 300 MHz NMR is:

a. 7.6 Hz
b. 15.2 Hz
c. 22.8 Hz
d. 30.4 Hz
13. (6 pts) The chemical shift for a peak due to a specific proton is 700 Hz downfield of TMS when analyzed using a 500 MHz NMR. What is the chemical shift (in Hz) for the same proton relative to TMS when analyzed on a 300 MHz NMR?

\[ 700 \left( \frac{500}{300} \right) = 420 \text{ Hz} \]

14. (10 pts) Use the chromatographs below to answer the following questions. The two chromatograms of samples containing A, B, and C were obtained at the same flow rate with two columns of equal length.

Which column has more theoretical plates? (Column 2)

Which compound has the smallest partition coefficient? (A)

Which column gives better resolution? (Column 1)

If these were HPLC columns, which column has smaller particles? (Column 1)

15. (10 pts) Give the two major factors that contribute to separation (resolution) in chromatography.

1. differential partitioning
2. band broadening