1. The first step in this problem is to convert the wavelength, \( \lambda \), to a frequency, \( \nu \), and then calculate the energy of the photon using \( \varepsilon = h\nu \). In such problems you must take care to use a consistent set of units. We will use S.I. units. Thus,

\[
\lambda = 18900 \text{ Å} = 18900 \times 10^{-10} \text{ m} = 1.89 \times 10^{-6} \text{ m}
\]

The frequency associated with this wavelength is given by:

\[
\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1.89 \times 10^{-6} \text{ m}} = 1.59 \times 10^{14} \text{ s}^{-1}
\]

The energy \( \varepsilon \) associated with a photon of this frequency is:

\[
\varepsilon = h\nu = (6.626 \times 10^{-34} \text{ J s}) (1.59 \times 10^{14} \text{ s}^{-1}) = 1.05 \times 10^{-19} \text{ J}
\]

Note -- the ENERGY of this photon corresponds to a DIFFERENCE between energy levels of the H atom.

The energy levels for the H atom are given by:

\[
\varepsilon_n = (-21.8 \times 10^{-19} \text{ J}) / n^2 \quad \text{where} \quad n = 1, 2, 3, 4, \ldots
\]

Thus,

\[
\varepsilon_1 = -21.8 \times 10^{-19} \text{ J}; \quad \varepsilon_2 = -5.45 \times 10^{-19} \text{ J}
\]

\[
\varepsilon_3 = -2.42 \times 10^{-19} \text{ J}; \quad \varepsilon_4 = -1.36 \times 10^{-19} \text{ J}
\]

We now seek an ENERGY LEVEL DIFFERENCE which matches the energy of the photon.

We see that the electronic transition which gives rise to an EMITTED photon with energy \( \varepsilon = 1.05 \times 10^{-19} \text{ J} \) is:

\[
\text{n}_{\text{initial}} = 4 \rightarrow \text{n}_{\text{final}} = 3
\]

2. A series of spectral lines in emission is characterized by a common value of \( n_{\text{final}} \) -- i.e. the quantum number of the level at which the transition terminates. Since the 18900 Å line arises from a transition in which \( n_{\text{initial}} = 4 \) and \( n_{\text{final}} = 3 \), the series to which it belongs is characterized by \( n_{\text{final}} = 3 \). The series limit for this series of emission lines is the wavelength that would correspond to the transition \( n_{\text{initial}} = \infty \) to \( n_{\text{final}} = 3 \).

From the energy level expression given in problem1 we see that:

\[
\varepsilon_{\infty} = (-21.8 \times 10^{-19} \text{ J}) (1/\infty^2) = 0
\]
Recall from lecture, that this energy corresponds to an ionized H⁺........e⁻ pair both at rest and infinitely separated

From problem 1, \( \varepsilon_3 = -2.42 \times 10^{-19} \text{J} \)

Thus, \( |\Delta E| = |\varepsilon_3 - \varepsilon_\infty| = |-2.42 \times 10^{-19} - 0| = 2.42 \times 10^{-19} \text{ J} \)

Here the vertical lines indicate that we are taking the \text{ABSOLUTE} value i.e. just the magnitude. Of course, for emission processes in which the \text{ENERGY OF THE ATOM IS LOWERED}, \( \Delta E < 0 \)

\[ \therefore \lambda = \frac{hc}{\Delta E} = \left\{ \frac{6.626 \times 10^{-34} \text{ J s}}{(3.00 \times 10^8 \text{ m s}^{-1})} \right\} / (2.42 \times 10^{-19} \text{ J}) \]

\[ = 8.21 \times 10^{-7} \text{ m} = 821 \times 10^{-9} \text{ m} = 821 \text{ nm} = 8210 \text{ Å} \]

The energy associated with a photon of wavelength \( \lambda = 8210 \text{ Å} \) is the energy required \text{TO IONIZE} an electron from the \( n = 3 \) state of the H atom.

3. The relevant electronic configurations for S and Cl are:

S: 1s²2s²2p⁶3s²3p⁴; Cl: 1s²2s²2p⁶3s²3p⁵

For both these atoms the most loosely bound electron is removed from a doubly-occupied 3p orbital on ionization.

Since 3p electrons in both S and Cl are predominantly screened \text{ONLY} by electrons of \text{LOWER PRINCIPAL QUANTUM NUMBER}, \( \text{Z}_{\text{eff}}(3p \text{ in S}) < \text{Z}_{\text{eff}}(3p \text{ in Cl}) \). Thus, the increasing value of \( \text{Z}_{\text{eff}} \) will make the first ionization energy of chlorine, \( I_1(\text{Cl}) \) is greater than \( I_1(\text{S}) \). Even though electron repulsion effects by other electrons with \( n = 3 \) will tend to aid the ionization process, they will make similar contributions for S and Cl. Thus, the order based on a consideration of \( \text{Z}_{\text{eff}} \) is the appropriate one.

When an electron is added, in each case, it will go into a 3p orbital which already contains a single electron. Such an added electron will experience a \text{SMALLER} \( \text{Z}_{\text{eff}} \) for S than for Cl. From these considerations, the added electron in Cl will be bound \text{MORE TIGHTLY} than the added electron in S. In both cases, adding an electron will produce additional electron repulsion. However, this must be more than offset by the attractive force associated with \( \text{Z}_{\text{eff}} \). Thus the activation energy of chlorine, \( \varepsilon(\text{Cl}) \) is greater than \( \varepsilon(\text{S}) \).
4. Photons of 274 nm are at the threshold for electron ejection. The energy of a 274 nm photon is the work function. **The work function is the energy $h\nu_0$, the threshold energy.** Use Planck's Law

$$E = \frac{hc}{\lambda} = \frac{(6.62 \times 10^{-34} \text{J}\cdot\text{s}) \left(3.00 \times 10^8 \text{ms}^{-1}\right)}{274 \times 10^{-9} \text{m}} = 8.64 \times 10^{-19} \text{J}$$

The expression developed by Einstein will provide the kinetic energy of electrons ejected by 100 nm photons

$$E = E_0 + \frac{1}{2}mv^2$$

$$\frac{(6.62 \times 10^{-34} \text{J}\cdot\text{s}) (3.00 \times 10^8 \text{ms}^{-1})}{100 \times 10^{-9} \text{m}} = 9.64 \times 10^{-19} \text{J} + \text{Kinetic energy}$$

Kinetic energy $= 1.12 \times 10^{-18} \text{J}$

$$\frac{1}{2}mv^2 = 1.12 \times 10^{-18} \text{J} = \left(\frac{1}{2}\right)(9.109 \times 10^3 \text{J}) v^2$$

$$v = 1.57 \times 10^6 \text{ms}^{-1}$$

5. These are one electron systems and ionization implies excitation of an electron to "$n=\infty$", that is, removal of the electron so that there is no attraction to the nucleus. The ionization energy is just the Rydberg energy.

$$E = (+2.18 \times 10^{-18} \text{J})Z^2 \text{ (must input energy to remove the electron)}$$

$$\text{He}^+: E = (2.18 \times 10^{-18} \text{J})(4) = 8.72 \times 10^{-18} \text{J}$$

$$\text{Li}^{2+}: E = (2.18 \times 10^{-18} \text{J})(9) = 1.96 \times 10^{-17} \text{J}$$

$$\text{Be}^{3+}: E = (2.18 \times 10^{-18} \text{J})(16) = 3.49 \times 10^{-17} \text{J}$$

$$\Delta E = (87.2 \times 10^{-19} \text{J}) / (1.60 \times 10^{-19} \text{J}) = 54.5 \text{ eV}$$

For $\text{Li}^{2+}$, $Z = 3$ and $\Delta e = 0 - (21.8 \times 10^{-19} (3^2/1^2) \text{ J}) = 196.2 \times 10^{-19} \text{J}$

in kJ mol$^{-1}$, $\Delta E = (196.2 \times 10^{-19} \text{J}) (6.02 \times 10^{23} \text{mol}^{-1}) = 11811 \text{kJ/mol}$

From the above equations we note that:

$$\Delta E_{\text{Li}} / \Delta E_{\text{He}} = Z^2_{\text{Li}} / Z^2_{\text{He}} = 3^2/2^2 = 2.25$$

We see that the numerical values confirm this ratio.

For $\text{Li}^{2+}$, in eV, $\Delta E = (2.25) (54.5) \text{eV} = 123 \text{eV}$

Using a similar approach for $\text{Be}^{3+}$ ($Z = 4$) we find:

$$\Delta E = 348.8 \times 10^{-19} \text{J} = 21 \text{kJ/mol} = 218 \text{eV}$$