

SOLUTIONS TO TOPIC E PROBLEMS

- 1) a) $6.12 \times 10^{14} \text{ sec}^{-1}$
b) $4.05 \times 10^{-19} \text{ J}$
c) 244 kJ/mol
d) 0.0410 moles of photons
e) 3.05 kJ
f) 6.17×10^{19}
- 2) a) $9.43 \times 10^7 \text{ sec}^{-1}$
b) 3.18 m
c) $3.18 \times 10^9 \text{ nm}$
d) $6.25 \times 10^{-26} \text{ J}$
e) 0.0000376 kJ/mol
- 3) a) 630 nm.
b) This wavelength falls in the visible spectrum, which runs (roughly) from 400 nm to 700 nm. (You are not required to memorize this, but it's nice to know.)
- 4) When an atom absorbs light, an electron moves from a lower level to a higher level.
- 5) a) $\Delta E = -2.960 \times 10^{-19} \text{ J}$
b) $\Delta E = +2.960 \times 10^{-19} \text{ J}$
c) -178 kJ/mol
d) 671.1 nm.
e) The wavelength we calculated in part d is within the visible spectrum, so visible light can move an electron from level 2 to level 3. (Of course the "visible light" must include the correct wavelength!)
- 6) We see many colors simultaneously because we always use samples that contain a vast number of atoms. With so many atoms, every possible transition between low-lying levels will be occurring in some of the atoms.
- 7) Level B \rightarrow level A:
 $\lambda = 1.9326 \times 10^{-6} \text{ m} = 1933 \text{ nm}$
The initial level for this transition is B and the final level is A.
- Level C \rightarrow level A:
 $\lambda = 6.1002 \times 10^{-7} \text{ m} = 610.0 \text{ nm}$
The initial level for this transition is C and the final level is A.
- Level C \rightarrow level B:
 $\lambda = 8.9140 \times 10^{-7} \text{ m} = 891.4 \text{ nm}$
The initial level for this transition is C and the final level is B.

8) $E_{\text{initial}} = -13.0 \text{ kJ/mol}$

9) $\lambda = 4.6080 \times 10^{-7} \text{ m} = 460.8 \text{ nm}$

10) a) $E = -82.06 \text{ kJ/mol}$.
b) $E = -2954 \text{ kJ/mol}$.

11) a) $n = 13$ for this level.
b) $n = 52$ for this level.

12) a) 5904 nm ,
infrared range
b) 236.2 nm , ultraviolet region.

13) a) $\Delta E = -6.9194 \times 10^{-20} \text{ J} (-41.67 \text{ kJ/mol})$
b) the value of n for the other energy level is 11.
c) the initial energy level for this transition.

14) a) $3.0 \times 10^6 \text{ m/sec}$
b) $1.9 \times 10^{-10} \text{ m} (190 \text{ pm})$
c) The uncertainty we have just calculated is certainly (pun totally intended) a significant fraction of 130 pm – in fact, our uncertainty is greater than 130 pm ! This means that the best possible measurement still leaves us with an uncertainty that is larger than the atomic radius – about all we can determine experimentally is that the electron is somewhere in the atom, which we already knew. Therefore, the Heisenberg Principle tells us that if we measure the velocity of the electron to an uncertainty of 10%, we will know virtually nothing about the position of the electron other than “it’s in the atom”.

15) E stands for the energy of the electron (or the overall electron energy, if there is more than one electron). ψ stands for the wave function that corresponds to the value of E .

16) A radial node is a **sphere** on which the electron can never be found. An angular node is a **plane** (or occasionally a double cone) on which the electron can never be found.

17) Here is the completed table, with the information you needed to figure out in red type.

Orbital	Value of n	Value of ℓ	Possible values of m_ℓ	Number of nodes	Number of radial nodes	Number of angular nodes
2p	2	1	-1, 0, 1	1	0	1
5d	5	2	-2, -1, 0, 1, 2	4	2	2
6p	6	1	-1, 0, 1	5	4	1
5f	5	3	-3, -2, -1, 0, 1, 2, 3	4	1	3
7d	7	2	-2, -1, 0, 1, 2	6	4	2
4p	4	1	-1, 0, 1	3	2	1
9f	9	3	-3, -2, -1, 0, 1, 2, 3	8	5	3

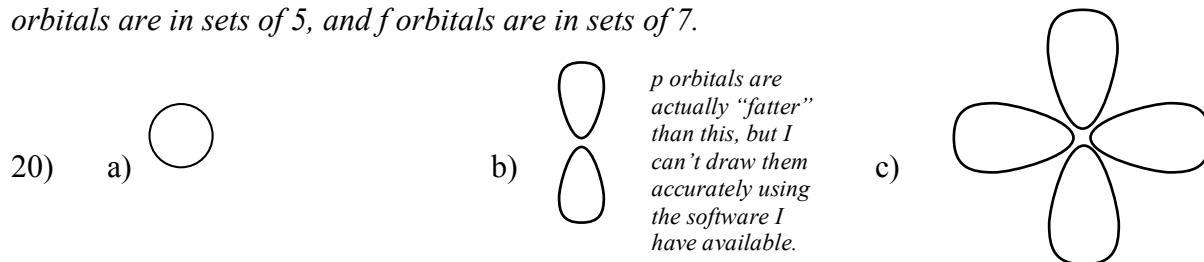
18) For any **hydrogen** orbital, the Bohr formula gives you the energy. (Careful, this equation only works here because this is hydrogen.) -52.52 kJ/mol

19) The number of orbitals in a specific subshell (i.e. orbitals with the same name) equals $2\ell + 1$.

a) For any p subshell, $\ell = 1$, so the number of 2p orbitals is $(2 \times 1) + 1 = \mathbf{3 \text{ orbitals}}$.

b) For any f subshell, $\ell = 3$, so the number of 5f orbitals is $(2 \times 3) + 1 = \mathbf{7 \text{ orbitals}}$.

It's simpler to just remember the pattern: s orbitals come in sets of 1, p orbitals are in sets of 3, d orbitals are in sets of 5, and f orbitals are in sets of 7.



- 21) a) A 2s orbital is larger than a 1s orbital (and the 2s has a higher energy).
b) A 2p orbital has two lobes, whereas a 2s orbital is a sphere.
c) A $2p_x$ orbital and a $2p_y$ orbital are oriented in different directions.
d) A 4d orbital is larger, has a higher energy and has more lobes than a 3p orbital.

- 22) a) **49 orbitals**
b) **15 orbitals.**
c) **1 orbital** has this combination.
d) **4 orbitals** that have the combination $n = 6$, $m_\ell = 2$.
e) There are **infinite orbitals** with this combination.

23) For a 4f electron (or any other f electron) $\ell = 3$, so the allowed values of m_ℓ are **-3, -2, -1, 0, 1, 2, or 3**. For any electron, regardless of the orbital, m_s can be **$-\frac{1}{2}$ or $\frac{1}{2}$** .

24) "The rules" say that ℓ must be smaller than n ... but there is a much better reason than "the rules." The number of nodes in any orbital is $n - 1$, so an orbital with $n = 3$ has 2 nodes. The number of angular nodes in any orbital is ℓ , so an orbital with $\ell = 3$ has 3 angular nodes. However, if an orbital has only 2 nodes, it cannot have 3 angular nodes!

25) a) The first graph (on the left side) is the electron density plot. There are two ways to determine this. First, electron density equals ψ^2 , so the y-axis label gives you the answer. Second, in electron density plots, the "humps" get smaller as you go out from the nucleus, whereas in radial probability plots, the "humps" get larger.

b) The most probable distance is around **1200 pm**. To get the most probable distance, you must look for the highest point on the radial probability graph (the graph of $\psi^2 \Delta V$).

c) This graph has **2 radial nodes**, because it has two places where the curve drops to zero. (Don't count the origin!)

d) This orbital **does have angular nodes**. You can tell by looking at the electron density plot; if it starts at the origin (0,0), the orbital has angular nodes.

e) This is a **4p orbital**. Since $n = 4$, this orbital must have three nodes. The graphs told us that the orbital has two radial nodes, so it must have one angular node ($3 - 2 = 1$). The number of angular nodes equals ℓ , so $\ell = 1$ for this orbital, making it a p orbital. Since $n = 4$, this must be a 4p orbital.

26) This is a **6p orbital**. The graph has four places where the radial probability drops to zero, which tells you that this orbital has four radial nodes. The problem says that the orbital is a p orbital, which means that $\ell = 1$, and that means that the orbital has one angular node. Therefore, it has five nodes in all. Since the number of nodes equals $n - 1$, n is 6 for this orbital, making it a 6p orbital.

27) a) The left-hand graph is the 3d orbital and the right-hand graph is the 2p orbital. You can tell by looking at where the electron density becomes insignificant. On the left-hand graph, that happens around 800 pm, whereas on the right-hand graph, that happens around 500 pm. Therefore, the left-hand graph represents a larger orbital. The 3d orbital is larger than the 2p, so the left-hand graph must be the 3d.

b) The graphs both show one “hump” because both of these orbitals have no radial nodes. The 2p has one node ($n = 2$) and one angular node ($\ell = 1$ for any p orbital), so it has no radial nodes. The 3d has two nodes ($n = 3$) and two angular nodes ($\ell = 2$ for any d orbital), so it also has no radial nodes.

c) Both graphs start at the origin because both of these orbitals have at least one angular node. Angular nodes pass through the nucleus, so the electron density is zero at the nucleus.

d) Any s orbital (1s, 2s, 3s, etc.) is correct here, because s orbitals have no angular nodes ($\ell = 0$ for any s orbital). Therefore, the electron density is nonzero at the nucleus.

- 28) a) **-178 kJ/mol**
b) **672 nm**
c) **-53 kJ/mol**

- 29) a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ or **[Kr]5s¹**
b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ or **[Kr]**
c) $1s^2 2s^2 2p^6 3s^2 3p^4$ or **[Ne]3s²3p⁴**
d) $1s^2 2s^2 2p^6 3s^2 3p^6$ or **[Ne]3s²3p⁶** or **[Ar]**
e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$ or **[Kr]5s²4d¹⁰**
f) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$ or **[Kr]4d¹⁰**
g) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ or **[Ar]4s²3d⁷**
h) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ or **[Ar]3d⁷**
i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ or **[Ar]3d⁶**

Note that whenever you remove electrons from an atom to make a positive ion, the electrons always come from the orbitals that have the highest value of n . In the case of Cd, the electrons come from the 5s orbital ($n = 5$), not the 4d orbitals ($n = 4$). For Co, the first two electrons come from the 4s orbital ($n = 4$); the third electron comes from the 3d subshell, since there are no more $n = 4$ electrons.

30) a) In a hydrogen atom, the orbital energy depends only on the value of n . Therefore, the 3s and the 3p_x orbitals have **exactly the same energy**.

b) In any atom beyond H, the 3s and 3p subshells have different energies, with the 3p subshell having the higher energy. Therefore, **the 3p_x orbital has a higher energy** than the 3s orbital.

c) In a hydrogen atom, the orbital energy depends only on the value of n , so **the 4s orbital has a higher energy** than the 3d_{xy} orbital.

d) In an uncharged Mn atom, the 4s subshell is filled and the 3d subshell is not, so the 3d subshell has the higher energy. (If the 3d subshell were lower, all seven electrons would be in the 3d orbitals and the 4s would be empty.) Therefore, **the 3d_{xy} orbital has a higher energy** than the 4s orbital.

e) In Mn²⁺, all five of the outer-shell electrons are in the 3d orbitals, and the 4s orbital is empty. Therefore, **the 4s orbital has a higher energy** than the 3d_{xy} orbital.

31) The “normal” configuration that you write using the rules for filling orbitals is the ground state. A configuration is impossible if...

- it has the wrong total number of electrons for the atom, or
- it has too many electrons in a subshell (for example, 7 electrons in the 2p subshell), or
- it includes an orbital that does not exist.

All other configurations are excited states. An excited state has the correct number of electrons, but they are not in the lowest energy orbitals.

a) This is an **impossible configuration**. There is only one 1s orbital, which can only hold up to 2 electrons.

b) This is an **impossible configuration**, because “1p orbitals” don’t exist.

c) This is the **ground state**.

d) This is an **excited state**. It has the correct number of electrons, and it doesn’t have an impossible situation, but the outermost electron is not in the lowest available orbital.

e) This is an **excited state**, for the same reason as part d. (The 87f orbital exists; it just has a very high energy, so you don’t normally see it in an electron configuration.)

32) a) This is an **excited state**, because the electrons prefer to spread out among all three orbitals (Hund’s rule).

b) This is an **excited state**, because the two unpaired electrons prefer to have the same spin.

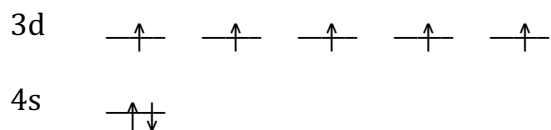
c) This is the **ground state**. It spreads the electrons out among all three orbitals, and the two unpaired electrons have the same spin, so it is the most stable possible arrangement.

d) This is an **impossible arrangement**, because it has two electrons in the same orbital with the same spin.

e) This is another way to show the **ground state**.

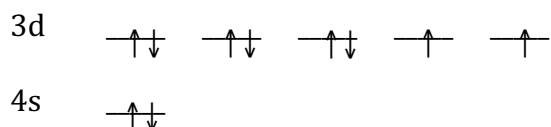
f) This is an **impossible arrangement**, because there are three electrons in one orbital.

33) a) Mn has the configuration $[\text{Ar}]4s^23d^5$. The five 3d electrons are in separate orbitals and have the same spin (according to Hund's Rule), so the energy diagram looks like this:

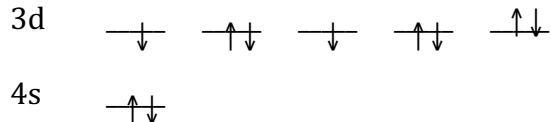


Note that you can also put the 3d electrons with their spins pointing downward, as long as they all point in the same direction.

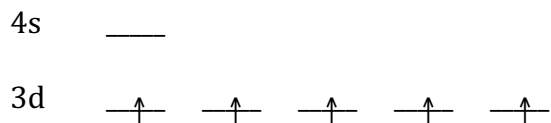
b) Ni has the configuration $[\text{Ar}]4s^23d^8$. The eight 3d electrons spread themselves out as much as possible (to give the maximum number of electrons with the same spin), so the energy diagram looks like this:



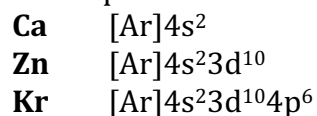
There are many other ways to arrange the 3d electrons, but you must have three pairs and two unpaired electrons, with the unpaired electrons having the same spin. For instance, the following is another legal answer:



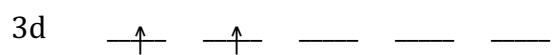
c) Mn^{2+} has the configuration $[\text{Ar}]3d^5$. Remember that the electrons with the highest value of n (the 4s electrons in this case) must be removed when you make a positive ion. In the ion, the 4s orbital has a higher energy than the 3d subshell (that's why the 4s orbital is empty), so the energy diagram looks like this (see next page):



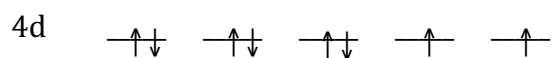
34) a) In order to have no unpaired electrons, an atom must have all subshells filled with electrons (or empty), because any partially filled subshell will obey Hund's Rule and spread out the electrons into different orbitals. The only atoms that have completely filled subshells in the fifth period are...



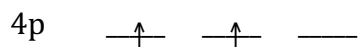
b) There are four possible ways to generate two unpaired electrons using the outer orbitals in the fourth period elements. One is to have two electrons in the 3d subshell, because these will spread out as follows:



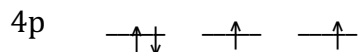
The second is to have eight electrons in the 3d subshell:



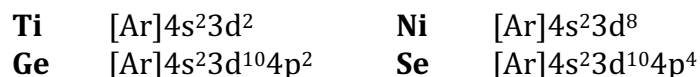
The third is to have two electrons in the 4p subshell:



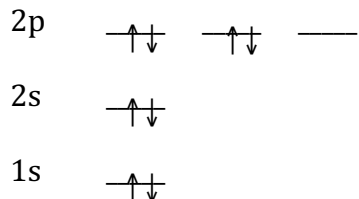
The fourth is to have four electrons in the 4p subshell:



Based on the normal order of filling orbitals, then, we expect four elements to have three unpaired electrons...

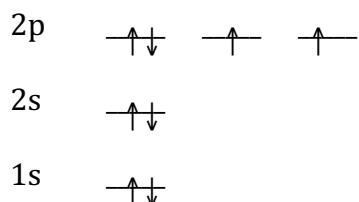


35) a) For an atom to be diamagnetic, all of its electrons must be paired, so the orbital energy diagram is:



(You can put the two pairs of electrons into any two of the three 2p orbitals.)

b) For an atom to be paramagnetic, it must have at least one unpaired electron, so the orbital energy diagram is:



(You can change the order of the electrons in the 2p orbitals, as long as you have one filled orbital and two half-filled orbitals in the 2p subshell.)

36) Paramagnetic substances have at least one unpaired electrons. Diamagnetic substances have no unpaired electrons (i.e. all electrons are paired up).

a) This configuration must have one unpaired electron (the 3s electron). Therefore, this configuration must be paramagnetic.

b) This configuration has all electrons paired, so it cannot possibly be paramagnetic. It must be diamagnetic.

c) This configuration must have one unpaired electron (the 3p electron), so this configuration must be paramagnetic.

d) This configuration could be paramagnetic (and it could also be diamagnetic). If the two 3p electrons are in the same orbital, the atom will be diamagnetic; if the two 3p electrons are in different orbitals, the atom will be paramagnetic.

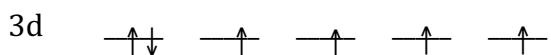
37) a) In a technetium atom, the 4s and 4p subshells are filled, and the 4d subshell has five electrons in it. There are two 4s electrons and six 4p electrons, so the total is $2 + 6 + 5 = 13$ **electrons**. (The complete configuration of Tc is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^5$)

b) Another way to say “how many electrons have $\ell = 1$?” is to say “how many p electrons are there?” For As, there are three sets of occupied p orbitals, the 2p, 3p and 4p subshells. The 2p and 3p subshells are full (6 electrons per subshell), and the 4p subshell has three electrons in it, so the total is $6 + 6 + 3 = 15$ **electrons**. (The complete configuration of As is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$)

c) In order to have $m_\ell = 1$, the value of ℓ for the orbital must be 1 or greater (i.e. a p, d, or f orbital). Checking the configuration of Kr, we see that there are four orbital types that have ℓ greater than or equal to 1: the 2p, 3p, 3d, and 4p orbitals. There are three 2p orbitals, and all of them are filled, but only one of them has $m_\ell = 1$ (the other two have $m_\ell = 0$ and -1). Likewise, there are three 3p orbitals, all of which are filled, but only one of them has $m_\ell = 1$; and there are three 4p orbitals, all of which are filled, but only one of them has $m_\ell = 1$. There are five 3d orbitals, all of which are filled, but once again, only one of them has $m_\ell = 1$ (the other four have $m_\ell = 2, 0, -1$ and -2). Therefore, we have exactly four orbitals in a Kr atom that have $m_\ell = 1$. Each orbital holds two electrons, giving us a total of **8 electrons**.

d) Exactly half of the electrons in Ra have $m_s = -1/2$! How can we tell? Every filled orbital contains one electron with $m_s = -1/2$ and one electron with $m_s = +1/2$. All of the orbitals in Ra are filled (the configuration is $[Rn]7s^2$), so we just divide the total number of electrons by two: $88/2 = 44$ **electrons**.

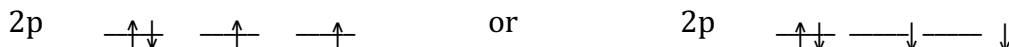
e)) In order to have $m_\ell = 2$, the value of ℓ for the orbital must be 2 or greater (i.e. a d or f orbital). This is similar to part c, but now we have to deal with the fact that the orbitals might not be filled. The configuration of iron is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. One of the 3d orbitals has $m_\ell = 2$. However, note that the 3d subshell for iron is not full; it looks like this:



The 3d orbital that has $m_\ell = 2$ might contain either one or two electrons. Therefore, the maximum number of electrons that have $m_\ell = 2$ is **2 electrons**. The minimum number is 1, by the way.

f) The configuration of oxygen is $1s^2 2s^2 2p^4$. The 1s and 2s orbitals each have one electron with $m_s = 1/2$, so we have two electrons there. As for the 2p subshell, it could look

like either of these diagrams (where upward-pointing arrows stand for electrons with $m_s = \frac{1}{2}$):



Based on this, we can see that there are two possibilities:

possibility #1: three 2p electrons with $m_s = \frac{1}{2}$ and one with $m_s = -\frac{1}{2}$

possibility #2: one 2p electron with $m_s = \frac{1}{2}$ and three with $m_s = -\frac{1}{2}$

Therefore, the total number of electrons that have $m_s = \frac{1}{2}$ must be either 5 ($2 + 3$) or 3 ($2 + 1$). Based on this, the minimum number of $m_s = \frac{1}{2}$ electrons is **3 electrons**.

38) a) Na has 11 protons in its nucleus, while Mg has 12. The higher nuclear charge on Mg pulls all of the outer-shell electrons inward, making Mg smaller than Na. *(The extra electron in the Mg atom would tend to make the atom larger, but the increased nuclear charge on Mg is the dominant factor.)*

b) The outermost electron in K is a 4s electron, whereas the outermost electron in Na is in the 3s orbital. The 4s orbital is larger than the 3s orbital, giving the Ca atom a larger atomic radius. *(The nuclear charge for K is much larger than it is for Na, which would tend to make K smaller, but the increased value of n for the outermost electrons is the dominant factor.)*

c) S^{2-} and Cl^- are isoelectronic: they have exactly the same electron configuration (the argon configuration). However, Cl has one more proton in its nucleus than S does. The higher nuclear charge in the Cl^- ion pulls all of the outer-shell electrons inward, making Cl^- smaller than S^{2-} .

d) Zr^{3+} and Zr^{4+} both have 40 protons in their nuclei. However, the Zr^{3+} ion has one more electron than the Zr^{4+} ion: Zr^{3+} has 37 electrons, while Zr^{4+} has 36 electrons. The additional electron in Zr^{3+} repels the other electrons in the outer shell, pushing them away from each other and making the outer-shell orbitals larger.

39) Ionization energies increase as you go from left to right and from bottom to top in the periodic table. As a result, we can make the following comparisons...

- The ionization energy of Al is larger than that of Ga, because Al is directly above Ga.
- The ionization energy of S is larger than that of Al, because S is to the right of Al.
- The ionization energy of Ne is larger than that of S, because Ne is above and to the right of S.

Therefore, the order is **Ga < Al < S < Ne**.

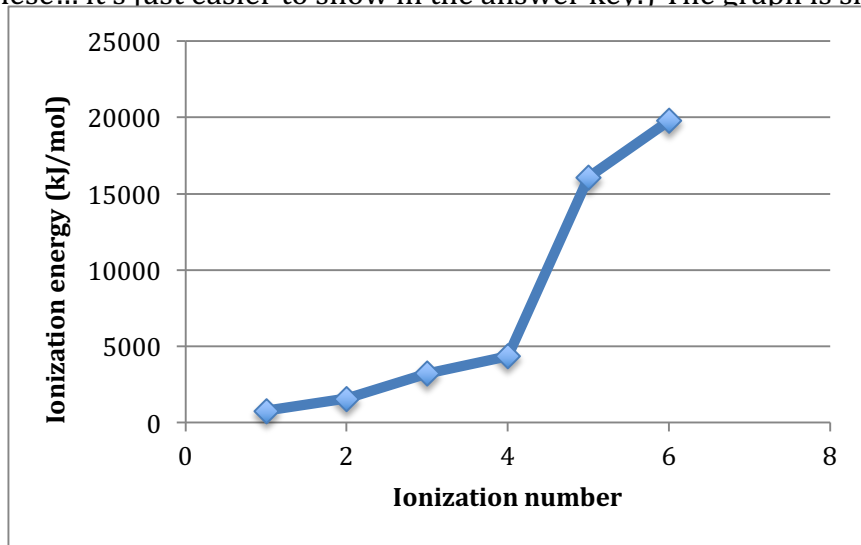
40) a) The ionization energies increase as you go from element 37 to element 40 because of the increasing nuclear charges. Adding a proton to an atom increases the attraction between the nucleus and the electrons, so it requires more energy to remove an electron.

b) Element 36 is an inert gas (Kr), in which the highest-energy electrons are in the 4p orbitals. When we move to element 37 (Rb), the next electron goes into the 5s orbital, which is much larger than the 4p and much less strongly attracted to the nucleus.

Therefore, the amount of energy required to remove an electron from Rb is much smaller than the energy needed to remove an electron from Kr.

c) The ionization energy of element 35 (Br) should be smaller than that of Kr, because Br has one fewer proton than Kr and both elements have their outermost electrons in the 4p orbitals. Therefore, the ionization energy of element 35 should be **lower than 1351 kJ/mol**.

41) If we graph these ionization energies, it's easier to see what's going on. (You **don't** have to graph these... it's just easier to show in the answer key.) The graph is shown below.



The first four ionization energies are rather low and increase gradually, but starting with the fifth, we see a big jump in the amount of energy required to remove each electron. This tells us that the first four electrons are outer-shell electrons, which are fairly easy to remove, but the subsequent electrons are coming from the inert-gas core. Since four electrons are easy to remove, the element must have exactly four electrons outside of its inert-gas core. The only element that fits this description in period 3 is **silicon (Si)**, which has the configuration $[\text{Ne}]3s^23p^2$.

42) The ionization energy is the energy required to remove an electron from the highest occupied orbital, which for chlorine is a 3p orbital. Therefore, $\Delta E = 1251 \text{ kJ/mol}$ for the transition from the 3p orbital to the ionized state, in which $E = 0$. This means that the energy of the 3p orbital must be -1251 kJ/mol , so the correct statement is:

"The energy of the 3p orbital in chlorine is -1251 kJ/mol ."