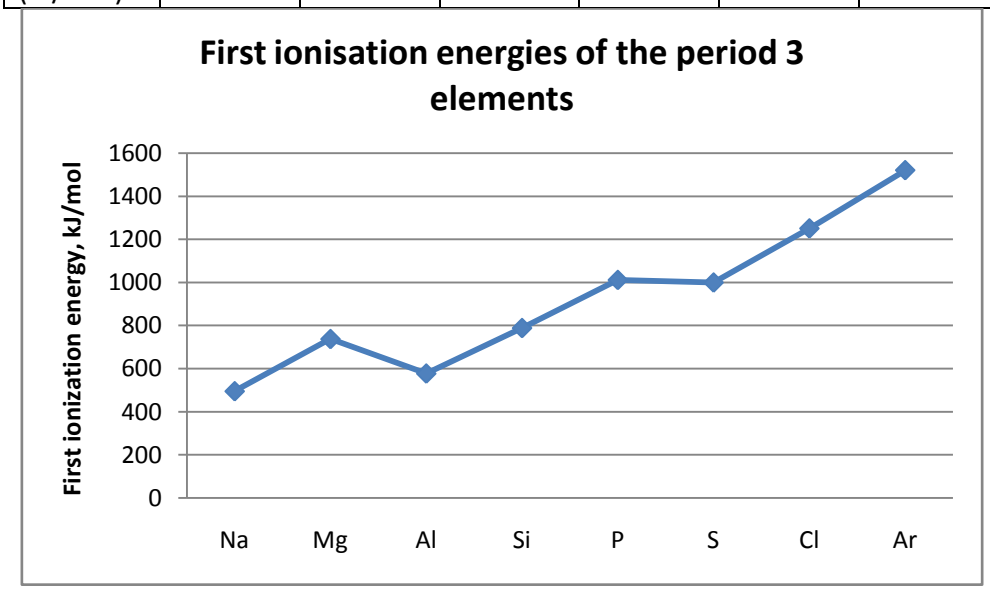
Question 1

3.a) Explain the reason for the variation of the first ionization energies of the third period elements.

Solution

	Na	Mg	Al	Si	P	S	Cl	Ar
First ionization energy (kJ/mol)	496	738	578	789	1012	1000	1251	1521



On this diagram we can see that the first ionization energy increases but there two drops: between Mg and Al and P and S. The explanation lies in the electronic structures of atoms.

Na $[Ne]3S^1$

Mg $[Ne]3S^2$

Al $[Ne]3S^23p^1$

We can see in atom of Al one more electron is added but it is added to the p orbital. P orbital is higher in energy than s orbital and electron on this orbital is further from the nucleus. The first ionization energy decreases 1) due to the screening effect of $3S^2$ electrons that reduces the pull from the nucleus and 2) due to the increased distance between 3p electron and nuclei that reduces attraction between them.

Si $[Ne]3S^23p^2$

P Al $[Ne]3S^23p^3$

S $[Ne]3S^23p^4$

We can see that three p orbitals in P atom are half- filled ($p_x^1 p_y^1 p_z^1$) whereas in S atom one p orbital is fully filled ($p_x^2 p_y^1 p_z^1$). The screening effect is the same for all p electrons, we remove an electron from the same p orbital (p_x) but for the pair of electrons repulsion exists therefore it easier to remove electron from the pair. For the next atoms (Cl and Ar) addition of one more proton has more influence on p electrons than repulsion between electrons of a pair.

Question 2

(4) b) Calculate the lattice energy (in Units kJ mol 1) for ZnO crystal using Eq. 3.4 based on electrostatic model and using a Born-Haber cycle. Compare the two answers and comment on any difference. Useful data: Medelung constant (A) = 1.6411 Born Constant (n) = 8 Internuclear distance (a) = 199 pm

$Zn(s) + ½\ O2(g) \rightarrow ZnO\ (s)\ \Delta H_f = -350.5$ kJ/ mol

$Zn(s) \rightarrow Zn(g)\ \Delta H_s = 130.4$ kJ/mol

$Zn\ (g) \rightarrow Zn^+$ I(Zn) = 906.3 KJ/mol

$Zn^+ \rightarrow Zn^{+2}$ $I(Zn^+)$ = 1733 kJ/mol

$1/2O_2(g) \rightarrow O\ (g)$ ½ ΔH_d = 248.5 kJ/mol

$O(g) \rightarrow O^-(g)$ EA(O)= 141 kJ/mol

$O^-(g) \rightarrow O^{-2}$ $EA(O^-)$ = 780 kJ/mol.

Solution

Find lattice energy value using electrostatic model.

$$\Delta U = N_A \cdot A \frac{Z_1 \cdot Z_2 \cdot e_0^2}{4\pi\varepsilon_0 a}(1 - 1/n)$$

Medelung constant (A) = 1.6411

Born Constant (n) = 8

Internuclear distance (a) = 199 pm = $199 \cdot 10^{-12}$m

$Z_1 = +2$

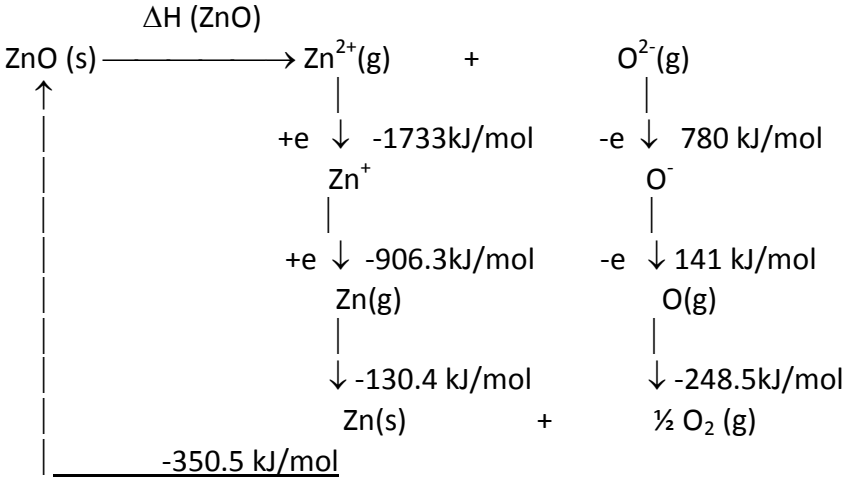
$Z_2 = -2$

$e_0 = 1.6022 \cdot 10^{-19}$ C

$\varepsilon_0 = 8.854 \cdot 10^{-12}$ C^2/m

$$\Delta U = 6.022 \cdot 10^{23} \cdot 1.6411 \frac{(1.6022 \cdot 10\text{-}^{19})^2 \cdot 2 \cdot (-2)}{4 \cdot 3.14 \cdot 8.854 \cdot 10^{-12} 199 \cdot 10^{-12}}(1\text{-}1/8) = 4012315 \text{ J/mol} = 4012 \text{ kJ/mol}.$$

Find lattice energy value using a Born-Haber cycle .



According to Hess Law $\Sigma\Delta H_i = 0$

ΔH (ZnO) = -(-1733-906.3-130.4-248.5+141+780-350.5)= 2447.7 kJ/mol.

We can see that lattice energy calculated using electrostatic model is 4012kJ/mol and when using a Born-Haber cycle lattice energy is 2447.7 kJ/mol. The accuracy of measuring of lattice energy using a Born-Haber cycle is limited by the accuracy of measuring of EA and I. Moreover good results were obtained only for singly charged ions, metal halides, metal hydride and noble gases. For ionic compounds good results are obtained when electrostatic model is used and we can see that 4012 kJ/mol is more close to the table meaning of lattice energy (4061 kj/mol), than 2447.7 kJ/mol.