Question #1

Born-Haber Cycle

Use Born-Haber cycles calculations to show why formation of the salt $MgBr_2$ is favoured over MgBr. Information you need (all in kJ/mol) to estimate the enthalpies of formation for the two salts:
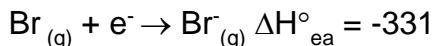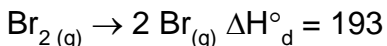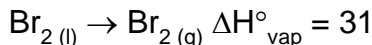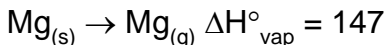
$Mg_{(s)} \rightarrow Mg_{(g)}$ $\Delta H°_{vap} = 147$ $Br_{2\,(l)} \rightarrow Br_{2\,(g)}$ $\Delta H°_{vap} = 31$

$Br_{2\,(g)} \rightarrow 2\,Br_{(g)}$ $\Delta H°_d = 193$ $Br_{(g)} + e^- \rightarrow Br^-_{(g)}$ $\Delta H°_{ea} = -331$

$Mg_{(g)} \rightarrow Mg^+_{(g)}$ $\Delta H°_{ie} = 737$ $Mg^+_{(g)} \rightarrow Mg^{+2}_{(g)}$ $\Delta H°_{ie} = 1450$
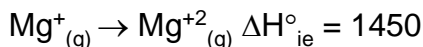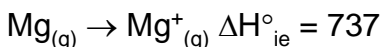
Use the Born-Mayer equation to estimate the lattice energies for each of the salts: the radius in Å for Mg is 1.60, the radius for Mg^+ is 1.16, the radius for Mg^{+2} is 0.72 and the radius for Br^- is 1.96. Assume that MgBr has a Rock Salt structure and that $MgBr_2$ has a Fluorite structure.

For MgBr (all in kJ/mol):

$\Delta H°_f = 147 + 737 + \frac{1}{2}(31) + \frac{1}{2}(193) + (-331) + U_0 = 665 + U_0$

$U_0 = [1390\,(1)(-1)\,1.748] / [1.96+1.16] \times [1-(0.345/3.12)] = -693$ kJ/mol

$\Delta H°_f = 665 - 693 = -28$ kJ/mol

For $MgBr_2$ (all in kJ/mol):

$\Delta H°_f = 147 + 737 + 1450 + 31 + 193 + 2 \times (-331) + U_0 = 1896 + U_0$

$U_0 = [1390\,(2)(-1)\,2.519] / [1.96+0.72] \times [1-(0.345/2.68)] = -2277$ kJ/mol

$\Delta H°_f = 1896 - 2277 = -381$ kJ/mol

Thus the increased lattice energy for the formation of $MgBr_2$ more than compensates for the energy of the second ionization enthalpy and $MgBr_2$ is favoured over MgBr. If we could make MgBr, it would spontaneously disproportionate (a redox reaction with itself) into Mg and $MgBr_2$:

$2MgBr_{(s)} \rightarrow Mg_{(s)} + MgBr_{2(s)}$ $\Delta H°_{rxn} = (-381 + 0) - 2 \times (-28) = -325$ kJ/mol
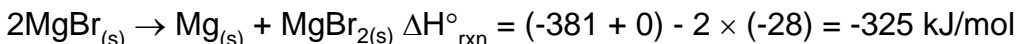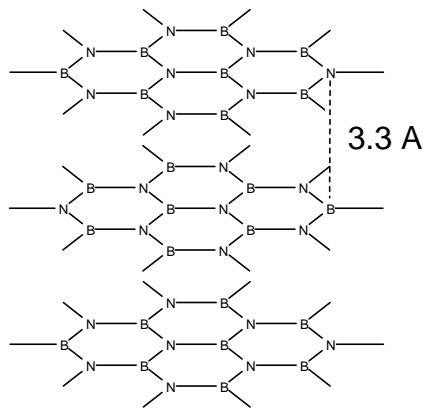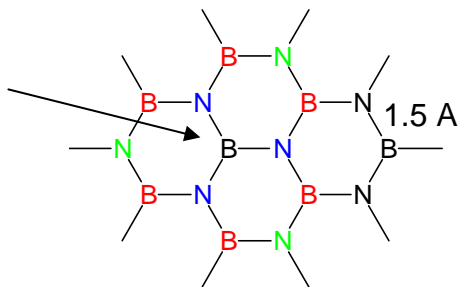
If you did not use the Madelung constant for fluorite for $MgBr_2$, you would get the wrong prediction.

Question #2
Madelung Constants
One form of boron nitride (BN) has a hexagonal layer structure similar to that of graphite. Assuming an ionic structure as pictured below answer the following questions:

a) what is the energy of attraction between a pair of adjacent B^{+3} and N^{-3} ions?

The energy of attraction between two ions is obtained from the Coulombic term:

E_{coul} = 1390 ($z_a \times z_b$)/d in KJ/mol if d is in Angstroms = 1390 (3)(-3)/ 1.5 Å = -8340 KJ/mol

You did not have to use the Madelung constant (it describes the arrangement of ions in the entire structure) or the short range repulsion term. The answer in J/pair of ions is $-1.48*10^{-17}$.

b) what are the **first three** terms in the expression for the Madelung constant for this arrangement?

The first 3 terms in the Madelung constant are found by finding the number and distance of closest neighbours, then the number and distance of next-closest neighbours etc. Thus, starting from the B indicated by the arrow:

A = [(3/1.5 Å) - (6/2.6 Å) + (3/3.0 Å)]
or, analytically with 1/d factored out: A = [(3/1) - (6/(2cos(30°))) + (3/2)]

You don't have to include the charges on the atoms because they are considered separately in the Born-Meyer equation. This is also why the terms in blue and green (that come from interactions between ions of opposite charge) are positive and the term coming from the interaction between ions with the same charge (red) is negative. The geometry is provided on the next page. Since the third term comes from a contact that is only 3.0 Å away (shorter than 3.3 Å), you don't have to consider the contacts with the adjacent layers.

c) how would the terms change in part b) if the adjacent layer had a boron-nitrogen distances of 2.7 Å instead of 3.3 Å?
If the layers were only 2.7 Å away, then the first three terms of the Madelung constant would be:

A = [(3/1.5 Å) - (6/2.6 Å) + (2/2.7 Å)] or, analytically A = [(3/1) - (6/(2cos(30°))) + (2/(2.7/1.5)]

The Madelung constant is only "constant" if the relative arrangement of the atoms remains the same.
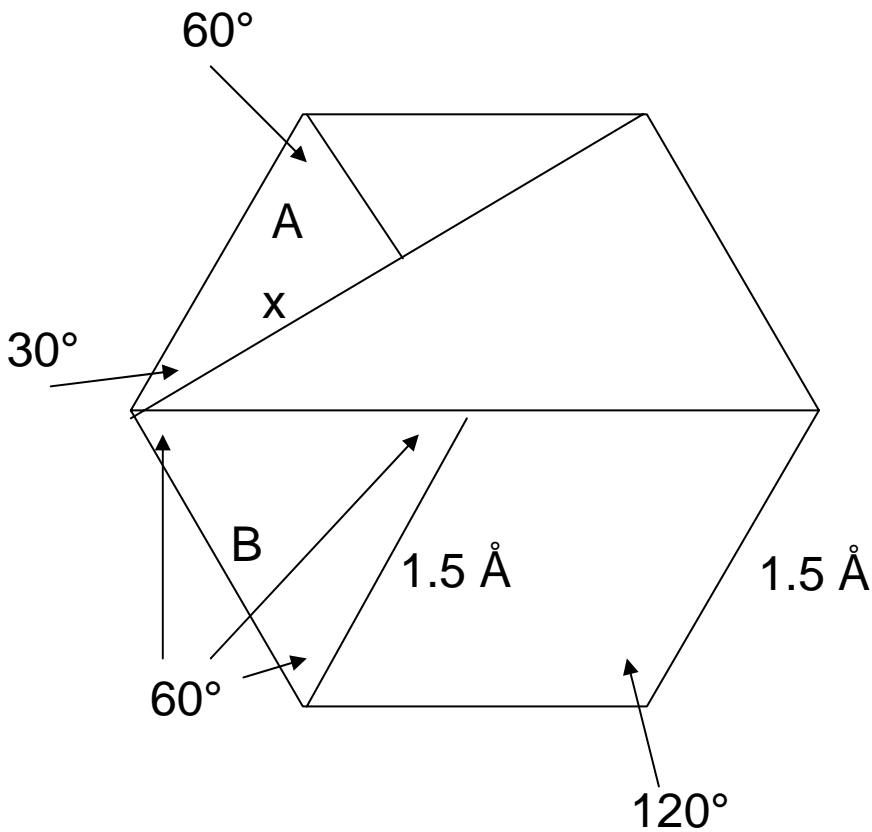
Geometry for question 2 (b):

Since the ions are arranged in a hexagonal array, you can find all the angles very easily. The angle at each point of the hexagon is 120°, so we know that half of that angle is 60°. The closest distance between adjacent atoms is already given (1.5 Å).

The next closest distance is found using the right triangle A, in which x = cos(30°)(1.5 Å) = 1.299 Å. Since the distance between the two closest B ions must be twice the distance x, the next closest distance is 2(1.299 Å) = 2.6 Å.

The third closest distance is the "diameter" of the hexagon, which is quickly provided by triangle B. Since we know that the angles in B must be 60°, this means that the triangle is equilateral with each side having a length of 1.5 Å. This means that the distance to the center of the hexagon is also 1.5 Å so twice that distance must be 3.0 Å.