Chemistry Investigation
Factors affecting percent differences between experimental and theoretical lattice enthalpies

Research Question

(1) Investigate the effect of covalent character of monovalent ionic salts on percent difference between Born-Haber lattice enthalpies and Kapustinskii theoretical lattice enthalpies.

(2) Extension: Investigate the effect of ionic radii differences of monovalent ionic salts on percent difference between Born-Haber lattice enthalpies and Kapustinskii theoretical lattice enthalpies

Exp: It is preferred to have a single research question, but there was a precedent in the TSM for a secondary data exercise to be extended with a supplementary RQ since the data is quite easy to gather.

Hypothesis

I hypothesize that as the difference in electronegativity between bonding atoms decreases, the percent difference between the lattice enthalpies of the Kapustinskii Equation and of the Born-Haber cycles will increase. This is because as the difference in electronegativity decreases, the covalent character of the crystal bonding increases, increasing the extent of electrostatic attraction unaccounted by the ionic model and decreasing the accuracy of the Kapustinskii theoretical values.

Similarly, I hypothesize that as the ionic radii difference between the cation and anion increases, the stronger the effect of polarization and the more distorted the ion becomes, causing the ionic model to deviate from the its assumption of perfectly spherical ions and increasing the percent differences.

Background Information

My idea for this exploration was inspired when we learned about theoretical and experimental lattice enthalpies. The theoretical lattice enthalpies were calculated from the **ionic model**, which assumes a completely ionic lattice, ignores any contribution from Van der Waal's attraction of ions, and assumes no covalent contribution.

Specifically, my Brown and Ford textbook reads the following as a method to calculate theoretical lattice enthalpies,
"To calculate the lattice energy for one mole, more ion interactions need to be considered as a solid crystal forms. The overall attraction between the positive and negative ions predominates over the repulsion of ions with the same charge as ions are generally surrounded by neighboring ions of opposite charge. This leads to the general expression $\Delta H^{o}_{lat} = Knm/(R_{Mn+}+R_{Xm-})$*, where K is a constant that depends on the geometry of lattice."*

Additionally, due to small inaccuracies deriving from the assumptions of the ionic model, it also reads that the theoretical lattice enthalpies differ slightly from the experimental Born-Haber lattice enthalpies, as described in *Excerpt 1*.

Excerpt 1: Brown and Ford textbook excerpt, from pg.183

Compound	ΔH_{lat}/kJmol^{-1} (Ionic model)	ΔH_{lat}/kJmol^{-1} (Born-Haber)	% Difference
NaCl	790	769	5.9
NaBr	754	732	8.3
NaI	705	682	9.4

Exp: Good justification for choice of topic.

This difference made me contemplate about the reliability and usefulness of models in chemistry, causing me to become more conscious of the differences between theory and reality. It made me question the importance in science on questioning sources and data, and trusting assumptions or models. To what extent has the knowledge I have learned in chemistry apply to the real world?

The philosopher Thomas Kuhn once proposed that the advancement of scientific knowledge results from successions of revolutions. He stated that they occur after a period of normal science, in which we view the world through a paradigm, which eventually experiences a paradigm shift over time for our perspectives evolve as scientific knowledge progresses. The Kapustinskii equation exemplifies one such model that has changed over time, deriving from the succession of Born-Mayer to Born-Landé equations. I desire to investigate the measure to which my knowledge applies as a reflection of reality. Hence my aim is to investigate the factors that produce differences in experimental lattice enthalpies, which reflect the reality around us, and theoretical lattice enthalpies, which model the reality we perceive.

However, I will not be using the proposed expression $\Delta H^{o}_{lat} = Knm/(R_{Mn+}+R_{Xm-})$ for my investigation. Instead, I will calculate theoretical lattice enthalpies using the Kapustinskii Equation, a formula outside my subject syllabus. Although there are several

PE: This is reflective TOK/NoS consideration. These connections support the personal interest - the student is really thinking about the topic.

other models to calculate theoretical values in addition to $\Delta H^{o}_{lat} = Knm/(R_{Mn+}+R_{Xm-})$, such as the Born-Landé equation, they all require information on the specific lattice geometry of the crystal, information which I discovered to be difficult to find/access. Hence, I decided to use the Kapustinskii equation for its practicality and ease of calculation, as it does not require knowledge on lattice geometry,

Exp: Justifying research question

The Kapustinskii equation is defined below, where $U_L = \Delta H^{o}_{lat}$

$$U_L = K * v * |z^+| * |z^-| / \langle r \rangle * (1 - d/\langle r \rangle) \qquad \text{[Equation 1]}$$

$K = 1.214 * 10^{6} * J * A * mol^{-1}$
$d = 0.345$ A
v = number of ions in empirical formula
z^+ & z^- = #s of elementary charge on cation and anion, respectively (ionic charge)
$\langle r \rangle = r^+ + r^-$, radii of cation and anion, respectively (A)

The ionic strength of the lattice is related to $v * |z^+| * |z^-|$, which calculates the number of ions in the empirical formula, and the ionic charge of the cation and the anion.

The size of the ions composing the lattice is related to the term $\langle r \rangle$, which defines the sum of the ionic radii of the anion and cation in the empirical formula. Note that the equation assumes perfectly spherical ions, for the calculations depend on thermochemical ionic radii.

The constant K describes the standard electrostatic conversion term, which defines a simplified version of the Madelung's constant in the Born-Landé equation. The Madelung's constant calculates the electrostatic attraction between all the surrounding ions in a lattice, and is measured as a sum to infinity (University of Sydney). It depends on crystal structure, thus changes accordingly to different lattice coordination numbers. However, Kapustinskii noticed that the Madelung's constant divided by the number of ions, v, is almost constant for many crystal structures. Hence, Kapustinskii equation can predict lattice enthalpies for ionic solids of unknown structures.

The term $(1 - d/\langle r \rangle)$ relates to the repulsion factor between ions of unlike charges within the lattice, which is unaccounted for by the K, the electrostatic conversion term. The repulsive force is small at large separations, but increases sharply when the ions come into contact. One method to calculate this behavior is to account for the compressibility of the crystal, where $d=0.345$ is the compressibility factor and $\langle r \rangle$, the sum of the ionic radii of the cation and the anion (University of Sydney). Note that crystal compressibility varies slightly according to its lattice.

Exp: The background information is quite lengthy (2 pages) but it remains relevant and aids understanding.

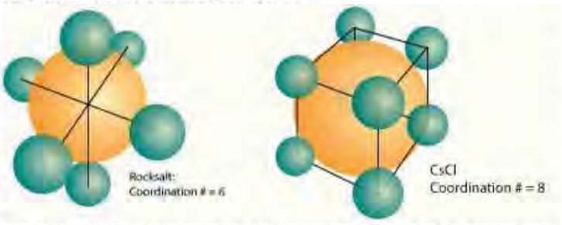
Covalent versus Ionic Character, background information for hypothesis

The difference between the covalent and ionic character of bonding may be descr orbitals. Covalent bonding involves the sharing of electrons between atoms—the overlap of orbitals allows the shared electrons to be concentrated in the region between two nuclei. Ionic bonding involves the transfer of electrons between atoms—atoms that assume completely ionic character do not involve any overlap of orbitals. However, polar covalent bonds tend to have some ionic character as electrons are being shared unequally between the atoms, thus affecting the degree of orbital overlap. Hence, bonding is better expressed as a continuum than two distinct types, a concept known as the **bonding continuum,** measured via differences in electronegativity—ionic compounds are distinguished by an electronegativity difference greater than about 1.8 (Brown, and Ford 109-120). Covalent character increases the percent differences between experimental and theoretical lattice enthalpies as the overlap of orbitals distorts the completely ionic lattice assumed by the Kapustinskii equation.

The Ionic Lattice

Ionic compounds are held together in predictable 3-D arrangements by the electrostatic attraction between every pair of ions of opposite charge within the lattice (University of Sydney). Ionic bonding extends throughout the structure in all directions—there are no individual ionic bonds. Note that ionic lattices consist of huge numbers of ions and may grow without end—they are usually expressed as a fixed ratio of the ions present. The lattice enthalpy is "the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions (Brown, and Ford 179).

Diagram 1: MX salt lattice geometries



*Note: Black guidlines serve to help visualize the lattice structure (the guidlines don't actually exist in lattice)

Different compounds adopt different geometric arrangements depending on their formula and radius ratio, namely the ratio of the ionic radius of the cation to the ionic radius of the anion. My investigation will explore monovalent ionic salts with formula MX, where M is the alkali metal and X is the halide. The ionic salts investigated will have rocksalt lattices of coordination number six, meaning that the number of ions directly adjunct to each ion is 6 (Saul). Exceptions to the rocksalt lattices include some cesium halides—CsF, CsCl, and CBr—which have Cesium Chloride lattice with coordination number 8 (Saul). These geometries have minimal differences in their Madelung's constant compared with other lattices—rocksalt lattice = 1.74756A and CsCl lattices = 1.76267A (University of Sydney)—thus also minimizing the effect the Kapustinskii equation may have when calculating lattice enthalpies of different lattice structures.

TOK: To investigate the importance in science on questioning sources and data, assumption, and models

Methodology

I will compare the lattice enthalpies derived from several databases to justify the values I obtain, and use Excel and Word to process the data. *Table 0.1* lists materials needed for this investigation.

Table 0.1 Equipment/Materials List

Databases	(i) IB Data Booklet ver. 2016 (ii) Wired Chemist (Data from *Huheey Inorganic Chemistry,* pps. 99-113) (iii) National Institute of Standards and Technology (iv) Knockhardy Publishing
Equipment	Excel document Microsoft Word

Justification of Selected Databases

(i) The IB Chemistry Data Booklet is my first choice for a database because it is a resource with easily obtainable experimental lattice enthalpies, as listed in Table 18, and because it would most likely have many people to cross check its data. As a data source used worldwide, due to the IB curriculum, I would assume its data is reliable because many people depend on it.

(ii) My second choice, Wired Chemist, traces to a reliable source called the *Huheey Inorganic Chemistry*, published by Pearson Education. However, it is important to note that the database itself is a tertiary source, and the provided information may not be recorded completely accurately.

(iii) My third choice of database derives from NIST, the National Institute of Standards and Technology. This is a federal science and technology website (from the United States), thus I assume the information to be reliable because it has verified experts cross checking its data. However, the information provided is not as complete as that from the IB Data Booklet, for it does not include information of lattice enthalpies for silver salts and a few other halides.

(iv) My fourth choice is Knockhardy Publishing, which is a reliable UK data source aimed towards producing notes and other resources for AS/A2 Level Chemistry. However, like NIST, it contains fewer data values for experimental lattice enthalpies—making Knockhardy my fourth choice of database.

Exp: Student considering reliability of data.

Variables

IV	Difference in electronegativity between anion and cation; Alkali metal for selected MX lattices, where X ∈ {F, Cl, Br, I}; Sum of thermochemical ionic radii of cation and anion;
DV	Difference in experimental and theoretical lattice enthalpies, use *Equation 2*
C	• Experiments performed at 298K; • Comparison of MX lattices • Effective nuclear charge: Increases across a period but remains relatively constant down a group. The investigation will compare lattice enthalpy trends for different alkali halides. This variable must be controlled because effective nuclear charge affects electronegativity—the higher values for effective nuclear charge increases electronegativity because the atom then has a stronger tendency to attract a bonding pair of electrons.

Range of Values for Independent Variable

The range for the electronegativity difference will derive from the following combination of alkali metals and halogens for MX alkali halides:

- Alkali metal (M) ∈ {Li+, Na+, K+, Rb+, Cs+}
- Halogen (X) ∈ {F-, Cl-, Br-, I-}
- *Extension*: silver halides, where halogen ∈ {F-, Cl-, Br-, I-}

Exp: Establishing sufficiency of data.

Justification for Range of Values

The range of alkali halides producing the independent variable is chosen due to the availability of data for experimental lattice enthalpies. Better availability of data would allow for a wider range of databases to choose from, and provide a standard of comparison between selected sources to ensure reliability. Moreover, the selected range creates a combination of 20 alkali halides, including the extension of the additional 4 silver halides, which will allow for collection of suitable relevant results.

Procedure

Com: Clearly described procedure

1. Calculate independent variable, electronegativity difference between cation and anion, for selected MX alkali halides (refer to **Range of Values for Independent Variable**), using data obtained from IB Data Booklet ver. 2016.
2. Find experimental lattice enthalpies (experimental lattice enthalpies can only be determined through Born-Haber cycles) from online databases. Ensure to find lattice enthalpies from various sources to justify reliability.
    a. Collect listed experimental lattice enthalpies directly from IB Data Booklet ver. 2016, Wired Chemist, and Knockhardy Publishing.
    b. NIST database does not directly list experimental lattice enthalpies, but it does provide raw data such as enthalpy of formation of alkali halides, atomization energy, energy of ionization, and electron affinity. Calculate experimental lattice enthalpies using Born-Haber cycles and the equation below:

$$\Delta H^{o}_{lat}\ (Born\text{-}Haber) = -\Delta H^{o}_{f}\ alkali\ halide\ +\ E_{at}\ alkali\ metal\ +E_{at}\ halogen\ +E_{io}\ alkali\ metal + E_{a}\ halogen$$

3. Use Kapustinskii Equation (refer to *[Equation 1]*) to calculate theoretical lattice enthalpies.
    Manipulation of variables:
    a. Obtain data for thermochemical ionic radii from IB Data Booklet ver. 2016, to calculate $\langle r \rangle = r^{+} + r^{-}$, the sum of the ionic radii of the cation and of the anion.
    b. $v * |z^{+}| * |z^{-}| = 2*|1|*|-1| = 2$, because MX lattices always have 2 ions in its empirical formula, and alkali halides always have +1 and -1 charge for cation and anion, respectively.
4. Calculate percent difference between theoretical and experimental lattice enthalpies using equation:

$$(theoretical\text{-}experimental)/experimental\ x\ 100\% \qquad [Equation\ 2]$$

    **Note: the percent differences divide the value difference by the experimental because the aim of the investigation is to explore the extent to which a model (theoretical) is a reflection of reality (experimental).*
5. Create graph for different MX lattices, comparing differences in electronegativity and percent difference between theoretical and experimental lattice enthalpies;
    a. x-axis: difference in electronegativity of bonding ions
    b. y-axis: percent difference between theoretical and experimental lattice enthalpies
6. **Extension:** Create graph for MX lattices, comparing differences ionic radii and percent difference between theoretical and experimental lattice enthalpies;
    a. x-axis: difference in ionic radii of bonding ions
    b. y-axis: percent difference between theoretical and experimental lattice enthalpies

Safety Considerations

Exp: Not much more could be said on safety.

It is assumed that the procedures taken by each database have considered safety issues, such as use of properly maintained equipment, safe control of heat loss from any exothermic reactions involved, or appropriate safety apparatus. However, this investigation does not require additional safety precautions needed for experimental procedures have already been performed by the database.

Raw Data

Table 1: Calculation of Dependent Variables, Raw Data

	Electronegativity	Ionic radii (A)
Group 1 alkali metal		Cation, charge 1+
Li	1.0	0.76
Na	0.9	1.02
K	0.8	1.38
Rb	0.8	1.52
Cs	0.8	1.67
Ag	1.9	1.15
Group 7 halogen		Anion, charge 1-
F	4.0	1.33
Cl	3.2	1.81
Br	3.0	1.96
I	2.7	2.20

Table 2: NIST Experimental Lattice Enthalpies, Raw Data (for Born-Haber Calculations)

Salt	$\Delta H_f°$ KJ/mol	E_{at} alkali metal KJ/mol	E_{at} halogen KJ/mol	E_{io} alkali KJ/mol	E_a halogen KJ/mol
LiF	-340.79	159.3	158.8	520.22176	-328.1745
LiCl	-195.72	159.3	242.6	520.22176	-348.5748
LiBr	-153.97	159.3	192.8	520.22176	-324.5363
NaF	-290.45	107.5	158.8	495.84571	-328.1745
NaCl	-181.42	107.5	242.6	495.84571	-348.5748
NaBr	-143.93	107.5	192.8	495.84571	-324.5363
KF	-326.77	89.0	158.8	418.80991	-328.1745
KCl	-214.68	89.0	242.6	418.80991	-348.5748
KBr	-180.08	89.0	192.8	418.80991	-324.5363

* All NIST values above come from cccbdb.nist, with exception to E_{at} alkali values that come from webbook.nist.

Processed Data [Note: Calculations for processed data are listed below data tables]

Table 3: Calculation of Dependent Variables, Processed Data

Salt	Electronegativity difference	Ionic radii sum <r> (A)	Ionic radii difference (A)	Radius ratio (r+/r-)
LiF	3.0	2.09	0.57	0.57
LiCl	2.2	2.57	1.08	0.41
LiBr	2.0	2.72	1.20	0.39
LiI	1.7	2.96	1.44	0.35
NaF	3.1	2.35	0.31	0.77
NaCl	2.3	2.83	0.82	0.55
NaBr	2.1	2.98	0.94	0.52
NaI	1.8	3.22	1.18	0.46
KF	3.2	2.71	-0.05	1.04
KCl	2.4	3.19	0.46	0.75
KBr	2.2	3.34	0.58	0.70
KI	1.9	3.58	0.82	0.63
RbF	3.2	2.85	-0.19	1.14
RbCl	2.4	3.33	0.32	0.83
RbBr	2.2	3.48	0.44	0.78
RbI	1.9	3.72	0.68	0.69
CsF	3.2	3.00	-0.34	1.26
CsCl	2.4	3.48	0.17	0.91
CsBr	2.2	3.63	0.29	0.85
CsI	1.9	3.87	0.53	0.76
AgF	2.1			
AgCl	1.3			
AgBr	1.1			
AgI	0.8			

Table 4: Lattice Enthalpies, Processed Data

Salt	Theoretical (Kapustinskii) (KJ/mol)	Experimental (calculated from Born-Haber) (KJ/mol)					
	Kapustinskii	(i)IB Data Booklet	(ii) Wired Chemist	(iii) NIST	(iv) Knockhardy	Average values	Percent difference
LiF	969.95	1049	1009	771.5		1029	5.70%
LiCl	817.92	864	829	648.0		847	3.33%
LiBr	779.43	820	789	605.4		805	3.08%
LiI	724.66	764	734			749	3.21%
NaF	881.51	930	904	645.0	918	917	4.01%
NaCl	753.36	790	769	557.5	780	780	3.45%
NaBr	720.44	754	736	519.1	742	744	3.24%

NaI	673.25	705	688			697	3.45%
KF	781.88	829	829	585.8	817	825	5.45%
KCl	678.81	720	720	495.2	711	717	5.55%
KBr	651.86	691	691	459.8	679	687	5.34%
KI	612.85	650	650			650	6.06%
RbF	748.80	795	795		783	791	5.33%
RbCl	653.59	695	695		685	692	5.96%
RbBr	628.53	668	668		656	664	5.91%
RbI	592.16	632	632			632	6.30%
CsF	716.26	759	759			759	5.63%
CsCl	628.53	670	670			670	6.19%
CsBr	605.30	647	647			647	6.45%
CsI	571.46	613	613			613	6.78%
AgF	834.85	974	969			972	15.82%
AgCl	717.80	918	916			917	27.15%
AgBr	687.53	905	900			903	30.64%
AgI	643.98	892	895			894	38.09%

*The experimental lattice enthalpies from NIST are much lower than experimental values obtained from other databases, and are thus exempt from calculated average values and percent difference.

Sample Calculation

Diagram 2: Sample Born-Haber cycle for LiF

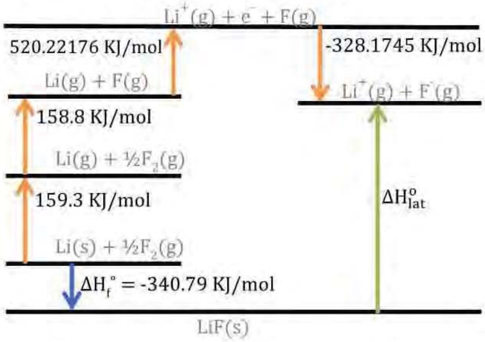


Table 2:
ΔH^{o}_{lat} (Born-Haber)
$= -\Delta H^{o}_{f}$ alkali halide + E_{at} alkali metal + E_{at} halogen + E_{io} alkali metal + E_{a} halogen

ΔH^{o}_{lat}(Born-Haber) of LiF
= -(-340.79KJ/mol) + 159.3KJ/mol + 158.8KJ/mol + 520.22176KJ/mol + -328.1745KJ/mol

ΔH^{o}_{lat}(Born-Haber) of LiF
= 771.5 KJ/mol

Ana: Final value inconsistent with work.

Table 3: Electronegativity difference = electronegativity alkali metal – electronegativity halogen
Electronegativity difference for LiF = 4.0 - 1.0 = 3.0

Table 3: Ionic radii sum = cation radius + anion radius
Ionic radii sum of LiF = 0.76A + 1.33A = 2.09A

Table 3: Ionic radii difference = anion radius – cation radius
Ionic radii difference for LiF = 1.33A - 0.76A = 0.57A

Table 3: Radius ratio = cation radius/anion radius
Radius ratio for LiF = 0.76A/1.33A = 0.57

Table 4: Theoretical lattice enthalpies, use Kapustinskii equation *(see background information)*
ΔH^{o}_{lat} of LiF = (-2*-1*1)/(0.76+1.33)A*1.214*(1-0.345/(0.76+1.33)A)*1000 = 969.95KJ/mol

Table 4: Percent difference = (experimental-theoretical)/experimental x 100%
Percent difference of LiF = (1029KJ - 969.95KJ)/1029KJ x 100% = 5.70%

Ana: This is only in part due to calculation error identified above so right to discard the NIST values based result ... and fortunately this means calculation error has not fed through to conclusion. This statement also helps build a picture towards evaluation since it is identifying a weakness.

Evaluation on Reliability of Data

The experimental data were cited with varying precision rangin evaluated by looking comparing the compounds where experimentally collected data is available. Looking at *Table 4*, there is generally a good agreement between the experimental values from the varying sources, though NIST values have been exempted from calculations due to producing significantly lower values than that of other sources. To calculate the uncertainty—which was not given for the calculated data sources (i), (ii), and (iv)—I calculated the standard deviation, and graphed it as error bars in *Fig.0.* As the error bars for each line of alkali halide do not overlap, with exception to LiCl and LiBr, the results are reliable and show clear trends in lattice enthalpies per type of MX compound.

Table 5: Standard Deviation Uncertainties

Salt	Standard Deviation Uncertainty, ±(KJ/mol)	Percent uncertainty	**Sample calculations**
LiF	28	2.7%	*Standard deviation uncertainty for LiF* $= \pm\sqrt{\sum(x-\bar{x})^2/(n-1)}$ $= \pm\sqrt{\sum((1049-1029)^2 + (1009-1029)^2/(2-1)}$ $= \pm 28\text{KJ/mol}$
LiCl	25	3.0%	
LiBr	22	2.7%	
LiI	21	2.8%	
NaF	13	1.4%	
NaCl	11	1.4%	
NaBr	9	1.2%	*Range of percent uncertainties:* $= largest\left(\frac{standard\ deviation\ uncertainty}{average\ experimental\ lattice\ enthalpy} * 100\%\right) -$ $smallest\left(\frac{standard\ deviation\ uncertainty}{average\ experimental\ lattice\ enthalpy} * 100\%\right)$ $= \left(\frac{25}{847} * 100\%\right) - \left(\frac{0}{632} * 100\%\right)$ $= 3.0\% - 0.0\%$
NaI	12	1.7%	
KF	7	0.8%	
KCl	5	0.7%	
KBr	7	1.0%	
KI	0	0.0%	
RbF	7	0.9%	
RbCl	6	0.9%	
RbBr	7	1.1%	
RbI	0	0.0%	
CsF	0	0.0%	
CsCl	0	0.0%	
CsBr	0	0.0%	
CsI	0	0.0%	
AgF	4	0.4%	
AgCl	1	0.1%	
AgBr	4	0.4%	
AgI	2	0.2%	

Ana: Standard deviation calculation on only two points is not really meaningful. Two data points can only describe a range while standard deviation quantifies the spread of data points around the mean.

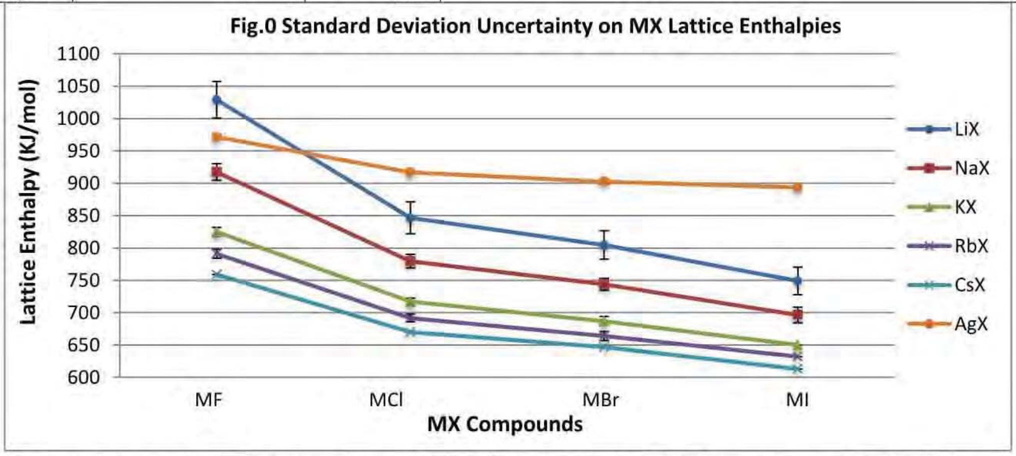


Fig.0 Standard Deviation Uncertainty on MX Lattice Enthalpies

The percent uncertainties for the compounds range 3.0%-0.0%, all of which is less than the percent errors calculated by the percent difference, meaning that any errors performed in obtaining lattice enthalpies lies with systematic errors.

Analysis and Discussion

Investigating alkali halides: Measure of covalent character

Com: Very ambiguous axis label. This graph is not clearly communicating overall

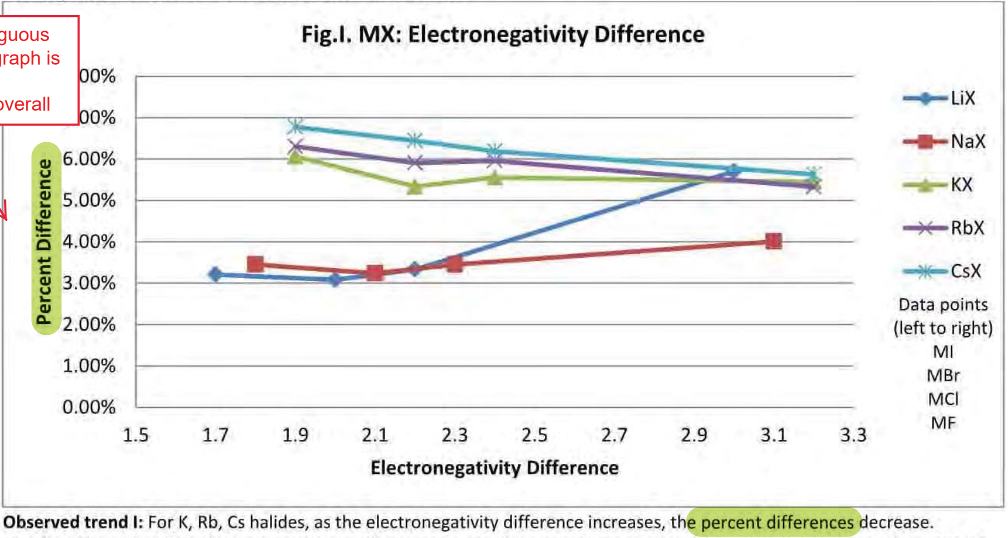


Fig.I. MX: Electronegativity Difference

Observed trend I: For K, Rb, Cs halides, as the electronegativity difference increases, the percent differences decrease. The ionic character of the lattice increases as electronegativity difference increases, and the percent differences decrease for the experimental lattice enthalpies adhere more closely to the ionic model, which assumes no covalent contribution. This hypothesis is further validated through an investigation on silver halides, which are generally covalent in character.

Com: Again ambiguous. Percent difference of what?

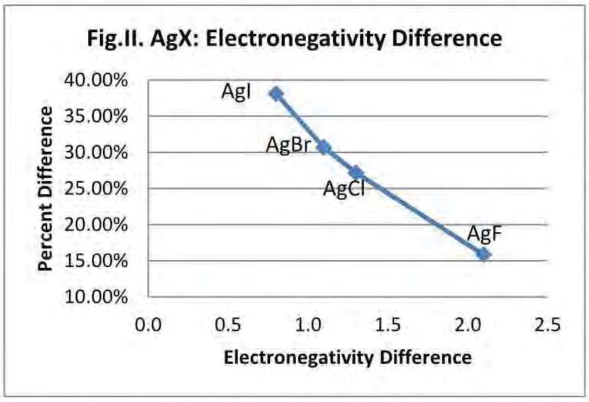


Fig.II. AgX: Electronegativity Difference

Extension A

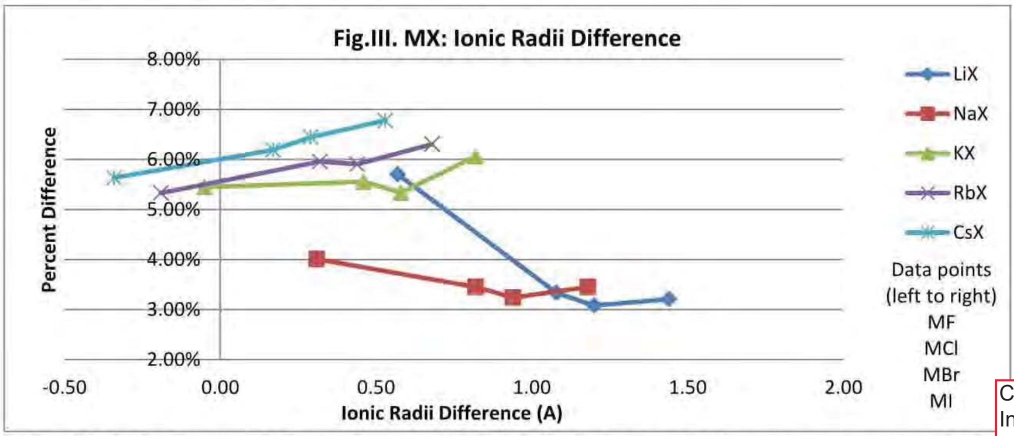
Lattice enthalpies of silver compounds exhibit particularly large percent differences, ranging approximately 15%-40%. This is likely due to the small electronegativity differences: AgCl, AgBr, and AgI have electronegativity differences smaller than 1.8, thus classify under covalent compounds. The Kapustinskii model overestimates the ionic contribution in the lattice enthalpy and underestimates the covalent contribution. AgF, which has an electronegativity difference of 2.1, portrays a much lower percent difference as it adheres more closely to the assumptions of the ionic model.

Hence, the ionic model, which accounts for ionic contributions only, is a poor tool to use to predict silver lattice enthalpies. Nevertheless, contrary to Observed Trend I, a different trend is observed for Li and Na halides, indicating that there must be another factor that plays a part in determining the accuracy of the theoretical model.

Observed Trend II: (For K, Rb, Cs halides) As the electronegativity difference increases, the percent differences decrease. Small alkali metals with small electron shells show a different trend: As electronegativity difference increases, the percent difference between the theoretical and experimental lattice enthalpies increases. Possible causes for the phenomenon may be due to either or both of the reasons stated below:

(i) The unaccounted contribution of Van der Waals forces, which increase in magnitude as the number of electrons on the atoms increases.

(ii) **Extension B:** The ionic radii differences for Li and Na compounds are noticeably larger than for the other group 1 halides, due to the small size of Li and Na cations. Note that the polarization of a compound increases when the size of the cation decreases or the size of the anion increases.



For Li and Na halides, the percent differences increase even though the electronegativity difference increases, observed in *Fig.* This is likely due to the covalent contribution/ion shape deviation from the polarization of the molecule. Given the cation's small size and the fact that it has few electrons to shield the nucleus, the anion exerts a strong attractive force on the electron in the electronegative atom of a neighboring molecule, polarizing the molecule causing the shape of the ions to deviate from the assumed spherical shape, causing inaccuracy thus increasing percent difference. [Note that the slight rise in trend for LiI and NaI is likely because the electronegativity difference for the compounds is smaller than 1.8 (refer to *Fig.I*), meaning that the bonding has strong covalent character that increases percent difference again.]

Com: Inappropriate terminology. These are ions, not molecules.

However, for compounds with an ionic radii difference smaller than about 0.40, the compounds appear to follow the same trend—as the electronegativity difference increases, the percent difference decreases. This trend likely persists because the covalent contribution is too minimal to make significant changes in the ionic character of the molecule. The ion shape deviation caused by large ionic radii differences thus also leads to a possible explanation for the slope of the percent differences for electronegativity differences: as the size of the anion increases to limited extent, the slope of *Fig.I* becomes increasingly negative due to decreased interference of polarization.

Extension C: Radius ratio

[Please refer to graph below this explanation] I observed that the percent difference for the alkali halides become particularly small around the 0.414 radius ratio, which is considered the ideal radius ratio for compounds of coordination number 6 (University of Sydney). The percent difference increases for radius ratios smaller and greater than 0.414, possibly indicating that the repulsion factor (which includes the term for compressibility factor) most accurately accounts for repulsion within lattices that adheres the most closely to the ideal radius ratio.

However, note that the ideal radius ratio of CsCl lattices is 0.732, which is quite close to the radius ratio of Cs halides, but Cs halides generally actually have higher percent differences than other alkali halides. This may be because the compressibility factor d is centered about 0.345 for all lattice geometries for the Kapustinskii equation, when in reality it differs slightly depending on lattice structure. CsCl structures may only have higher percent differences than rocksalt structures because they deviate further away from 0.345 than do rocksalt geometries.

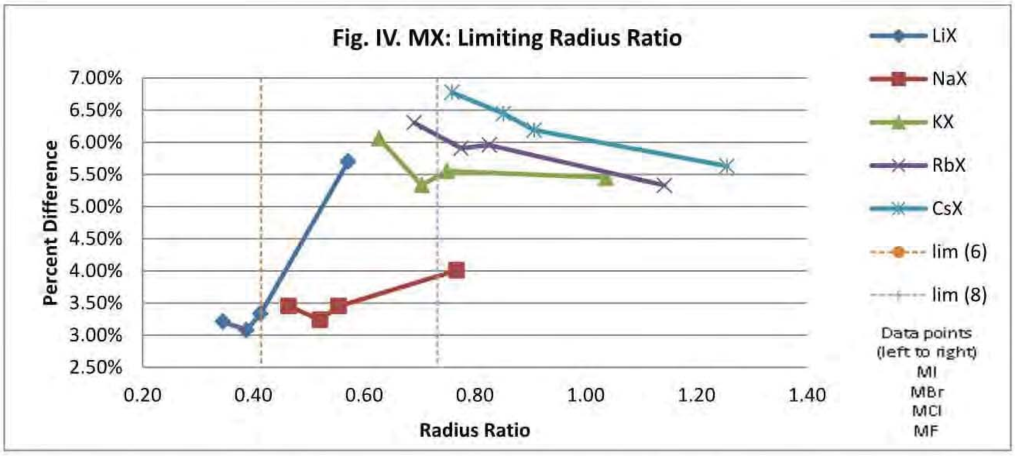


Fig. IV. MX: Limiting Radius Ratio

A speculation: The compressibility factor increases as the more ions fit around the central atom (radius ratio increases as coordination number increases. Also, as the cation size increases, more anions can fit around the cation without overlapping. This may justify why sodium halides experience the dip in percent differences beyond 0.414—as sodium halides have a larger cation size than that of lithium halides, the ideal radius ratio for sodium halides would also be slightly beyond 0.414. However, this is merely a speculation and more research is needed to justify the radius ratio reasoning behind this observation—thus marking an area of additional investigation.

An anomaly in the data

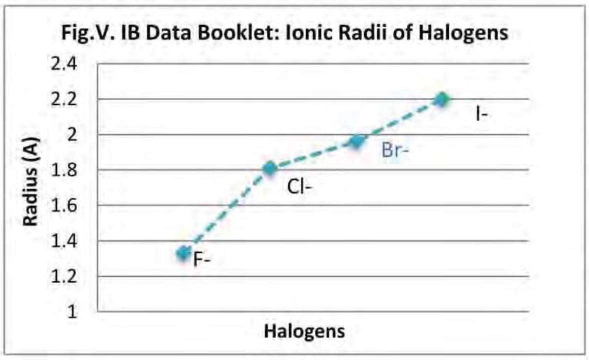


Fig.V. IB Data Booklet: Ionic Radii of Halogens

Any trend for MX compound has slight anomalies where X = Br. A possible explanation for the anomaly in trend for bromine in the ionic radii of halogens is seen in *Fig.V.* Perhaps the compression of the thermochemical ionic radii is calculated in a linear fashion, and since bromine deviates slightly off a linear trend, the theoretical lattice enthalpies for alkali bromides also deviate slightly. For rocksalt structures, this is observed as a slight dip in the theoretical lattice enthalpy trend; For CsBr, which follows CsCl structure instead of rocksalt, this may be observed instead as a slight bump in the trend.

Conclusion

(1) Investigate the factors that produce percent differences between Born-Haber experimental values and theoretical values, as derived from Kapustinskii Equation, for different lattice enthalpies.
    a. My hypothesize is valid for KX, RbX, CsX, and AgX lattices: As the difference in electronegativity between bonding atoms decreases, the percent difference between the lattice enthalpies of the Kapustinskii and Born-Haber will increase. This is because as the difference in electronegativity decreases, the unaccounted covalent contribution increases, thus decreasing accuracy of the theoretical lattice enthalpy.

(2) **Extension**: As ionic radii difference increases, percent difference increases: Ionic radii difference for small cations causes polarization of the ion, resulting in increasing percent difference as ions adhere less to the perfectly spherical shape of the model. Applicable for LiX and NaX lattices.
    a. Additionally, Li and Na halides appear to experience much less percent differences than compared to other alkali halides. This may be due to two factors:

Eva: Although the student is over-interpreting minor fluctuations he is at least trying to identify and explain trends at the appropriate level with suitable concepts.

   - i. Less covalent contribution from Van der Waals due to fewer electrons around cation.
   - ii. A radius ratio that adheres more closely to the ideal radius ratio of 0.414 of rocksalt coordination number 6 of many alkali halides. This is supported by graph *MX: Limiting Radius Ratio*, in which lithium and sodium halides have radius ratios significantly closer to 0.414 than the other alkali halides.
- b. Anomalies for alkali bromides: Perhaps the compression of the thermochemical ionic radii is calculated in a linear fashion, and since the ionic radii of bromine deviates slightly off a linear trend, the theoretical lattice enthalpies for alkali bromides also deviate slightly.

The conclusion for trend (a) can be justified through the clear differences between covalent and ionic lattices. The conclusion is further crosschecked by information drawn from the Brown and Ford textbook. However, conclusions drawn under **Extension** are speculations or considerations of other factors that may have affected the percent difference between lattice enthalpies. I have not been able to find sources that directly verify the conclusions for **Extension**; hence the reliability of its conclusions is more questionable.

Evaluation

Sources of error—apart from the limitations of the Kapustinskii equation drawn from the conclusion—may also derive from the simplified Madelung's constant or the compressibility of the lattice, for the Kapustinskii equations uses the simplified values for both numbers. Although obtaining the exact values for Madelung's constant or lattice compressibility would improve accuracy of the results, doing so would defeat the purpose of the investigation—to determine the reliability of the Kapustinskii Equation.

Moreover, I also speculated the reason for the abnormally high percent differences for data values from database NIST, coloured in blue, which were excluded from the averaged values used for the analysis. Possible reasons for this deviation include:

- Differences in methods of acquiring experimental data: especially when obtaining values for the enthalpy of formation, the difficulties in controlling heat loss and standard conditions contribute to inaccuracy of data. This would describe a systematic error.
- The values for the theoretical lattice enthalpies derive from the IB Data Booklet, meaning that they derive thermochemical ionic radii from only one source. This decreases the reliability of the obtained values for the theoretical lattice enthalpies, but since not all sources have data on thermochemical ionic radii (Knockhardy and NIST do not provide this information), I used the most reliable database—IB Data Booklet—to determine the theoretical values.

Eva: Overestimating these factors

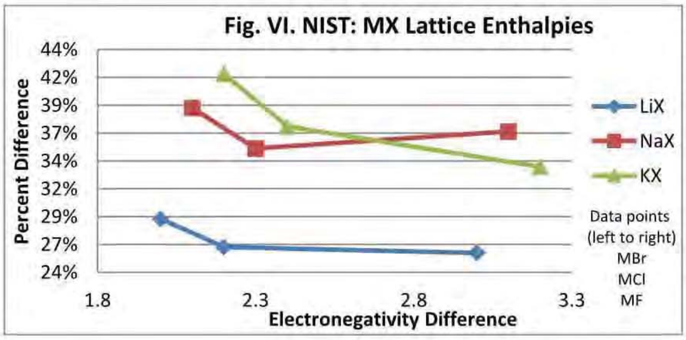


Fig. VI. NIST: MX Lattice Enthalpies

The considerably lower lattice enthalpies acquired from NIST also results in relatively higher percent differences between theoretical and experimental lattice enthalpies. However, similar trends are observed from NIST values as with data from other databases, as seen with *Fig. VI.*, further substantiating the possibility that the deviation roots from a systematic error in which different methods were used in acquiring the experimental data.

Improvements and Extension

Although I was unable to expand on my range of chosen halogens (X) for the selected lattices due to the lack of experimental data available, a wider range of halogens would produce more reliable trends in percent differences for each alkali metal—it would allow me to determine whether the trend in percent differences is linear or curved. A main limitation to my methodology is that it could not completely segregate the distinct variables affecting lattice enthalpies—for example, Li and Na halide trends were curved due to additional polarization. I feel like with a higher scientific understanding, I can deconstruct the Kapustinskii equation piece by piece and study how these variables affect *parts* of the equation. [Note that I have modified my procedure slightly by adding **Extension A** (Ag halides) and **Extension C** (radius ratio), in order to better justify my conclusions or analyze observed trends.]

Eva: Extensions given

Moreover, more accurate percent differences could have been derived if each source used to obtain lattice enthalpies had also provided data on ionic radii, rather than relying solely on IB Data Booklet ionic radii to determine the Kapustinskii theoretical lattice enthalpies. Another possible area of exploration is the percent differences produced when comparing MX_2 structures, as opposed to just MX, and to investigate the extent to which the geometry of the compound has an effect on the inaccuracies developed.

Eva: The suggestions that follow are more extensions than modifications.

If I were to improve the methodology of the experiment, I would investigate further in into the properties of bromine to determine other reasons for the slight deviation of the trend for alkali bromines. Additionally, I would also further investigate the effects of having an ideal radius ratio in determining accurate theoretical lattice enthalpies, and whether the radius ratio has direct links with the degree of concavity of the trends for percent differences.

Reflection on Models versus Reality

Scientific models are simplified representations of reality, developed as methods to visualize the natural world or facilitate calculation of theoretical data. Lattice enthalpies cannot be calculated directly and must be calculated via Born-Haber cycles; however, Born-Haber cycles require a lengthy series of steps. Using the Kapustinskii equation, which only needs knowledge of lattice formula and ionic radii, is much easier to use for predicting lattice enthalpies. However, it trades off ease of use with accuracy—the Kapustinskii uses approximated values such as compressibility factor or K constant, and higher percent differences are observed for lattices that do not adhere completely to its assumptions. Hence, the Kapustinskii equation is a good model to explain the principle factors composing lattice enthalpy (such as ionic radii and compressibility), but it is not a completely accurate representation of reality. It is always crucial to keep in mind that models only *simulate*, but not represent, reality.

Works Cited

Brown, Carin, and Mike Ford. *Higher Level Chemistry*. Malaysia: Pearson Education, 2009. Print.

Huheey Inorganic Chemistry. "Lattice Energies (E) for Common Compounds." *Wired Chemist*. Claude Yoder, n.d. Web. 22 Jan. 2016. <http://www.wiredchemist.com/chemistry/data/lattice-energies>.

International Baccalaureate Organization. *Chemistry Data Booklet First Assessment 2016*. N.p.: International Baccalaureate Organization, Feb. 2014. PDF.

Johnson, Russell D., III, ed. "Http://cccbdb.nist.gov/Intro.asp." *CCCBDB*. NIST, Sept. 2015. Web. 22 Jan. 2016. <http://cccbdb.nist.gov/Intro.asp>.

Lattice Enthalpy. N.p.: Knockhardy Publishing and Jonathan Hopton, 17 June 2011. PDF.

NIST. "NIST Chemistry WebBook." *NIST WebBook*. U.S. Secretary of Commerce, n.d. Web. 24 Feb. 2016. <http://webbook.nist.gov/>.

Sauls, Barbara L., and Frederick C. Saul. "Cesium Chloride Crystal Lattice." *Cesium Chloride Crystal Lattice*. King's College, n.d. Web. 24 Feb. 2016. <http://departments.kings.edu/chemlab/animation/cscl.html>.

Sauls, Barbara L., and Frederick C. Sauls. "Sodium Chloride Crystal Lattice." *Sodium Chloride Crystal Lattice*. King's College, n.d. Web. 24 Feb. 2016. <http://departments.kings.edu/chemlab/animation/nacl.html>.

University of Sydney. "E12 Understanding Crystal Structures." *School of Chemistry*. School of Chemistry, n.d. Web. <https://scilearn.sydney.edu.au/fychemistry/prelab/e12.shtml>.

END OF STUDENT REPORT