

The Thermodynamic Formation of Ionic Bonds Using the Born Haber Cycle Approach to Hess' Law to Explore Lattice Energy

by

Dr. Steve Carman, Professor of Biophysical Sciences and Facilitator, Human Cadaver Facilities,
Western Nevada College, Carson City Campus

reviewed and edited by

Dr. Gary Evett, Professor of Biophysical Sciences, Western Nevada College, Fallon Campus,

Dr. Elizabeth Tattersall, Instructor of Biophysical Sciences, Douglas Campus,

and

Mr. Devin Miner, CHEM 122 Student, Spring 2015

Student Name		Date	
Course and Section		Faculty Sign-Off	

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Introduction I

In order for ionic bonds to develop, there must be a reduction in the energy of the particles to form ionic compounds. The reduction in energy is associated with an increased stability of the compound.

"One of the most over-worked and mis-used words in chemistry is 'stability'. Yet it has a clear unambiguous meaning in the thermodynamic sense. ... [W]e shall treat stability on an energetic basis only, reserving the more complete aspect of the problem ..." [1]

for the lecture on Thermodynamics in General Chemistry II (CHEM 122 at WNC). In addition, more detail on "stability" will be discussed in the lecture on Elementary Reaction Rates in General Chemistry I (CHEM 121 at WNC).

"The heat liberated in an exothermic reaction (review the General Chemistry I lecture on Thermochemistry to refresh your memory on the terms described in this monologue) implies that the products have a lower enthalpy (heat content) than the reactants; hence we may state that the products are energetically stable with respect to the reactants." [2]

The enthalpy change during a reaction between a metal and a non-metal (to make a salt) is quite valuable. From the various enthalpy values involved in a simple reaction to produce a simple salt composed of a mono-valent cation and a mono-valent anion, we may determine an entity known as the lattice energy (this works for more complex salts, as well). The lattice energy is defined as the energy required to separate the ions from a crystal lattice to infinite distances (review the idea of lattices in the General Chemistry I lecture on States of Matter). The flip side of lattice energy is that it's a measure of the cohesion of the ions in a crystal lattice and is *"the energy released when the crystal is formed by bringing together the separate ions"*. [3]

The most stable ionic compounds form when lattice energies are very large or when elements with low ionization energies (metals; review the lecture in General Chemistry I on Modern Atomic Mechanical Theory for refreshing your understandings of ionization energies and electron affinities) react with elements with high electron affinities (non-metals).

Lattice energies also describe the ion-ion interaction strengths: as the charge of the ions increases, the lattice energy decreases. In addition, as the size of the ions increases, the lattice energy decreases. Ionic compounds with smaller lattice energies tend to be more soluble in

water. Ionic compounds with higher lattice energies require more thermal energy to boil and melt.

Lattice energies are not easily empirically determined as it's difficult to isolate gaseous ions: rather, lattice energies are calculated using Born-Haber cycle methodology, which is an application of Hess' Law.

"Hess's Law of Constant Heat Summation (or just Hess's Law) states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes. This law is a manifestation that enthalpy is a state function." [4]

More detail involving Hess' Law will be forthcoming in General Chemistry II lecture and in a lab experiment in CHEM 122, as well.

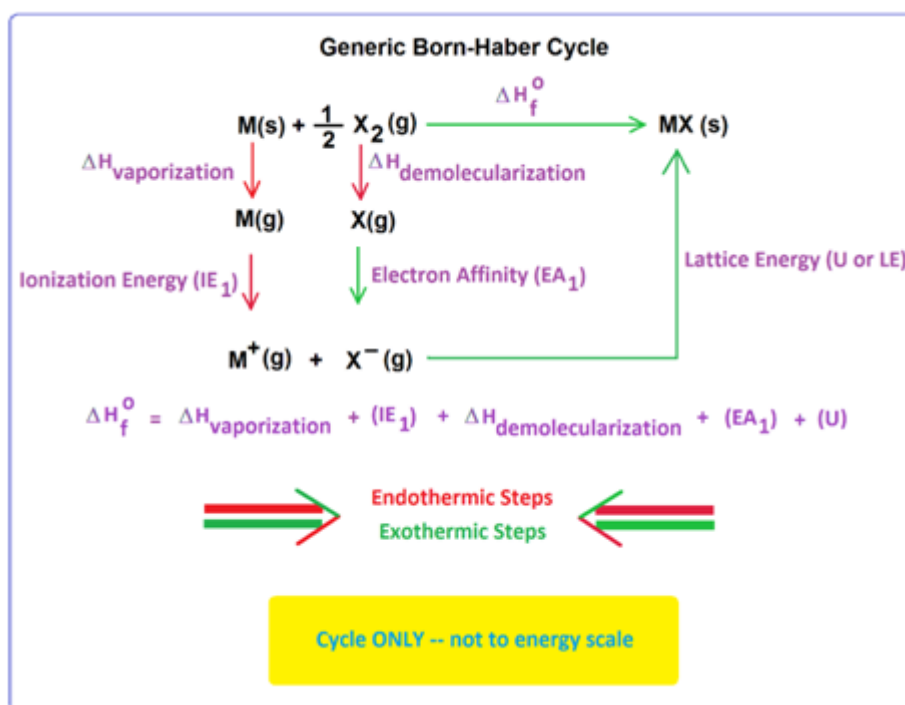
Introduction II

The analysis of reactions between metals and non-metals to generate a salt (an ionic compound) uses the Born-Haber Cycle: a series of reactions dependent upon energy that, when summed, provide a measure of the energy necessary to form the solid ionic compound, i.e., a reaction by parts,

where the total of the parts gives the overall reaction energy. Using Born-Haber, there are at least two different approaches, both of which give the same information. The simplest cycle of the two is as above (note that the arrows are color coded). This is a Born-Haber Cycle (Born-Haber I) for the reaction between any mono-valent cation (M) and any halogen (X) to form an ionic compound. Some defining of symbols would be helpful.

Reaction 1, indicated by the $\Delta H_{\text{vaporization}}$, is the energy of vaporization (some authors refer to it as sublimation) of the solid metal to the gaseous form of the metal. This step is endothermic, i.e., it absorbs energy.

Reaction 2, indicated by the $\Delta H_{\text{demolecularization}}$, is the decomposition of the molecular halogen to the atomic form (some authors refer to this as dissociation). This step is also endothermic.



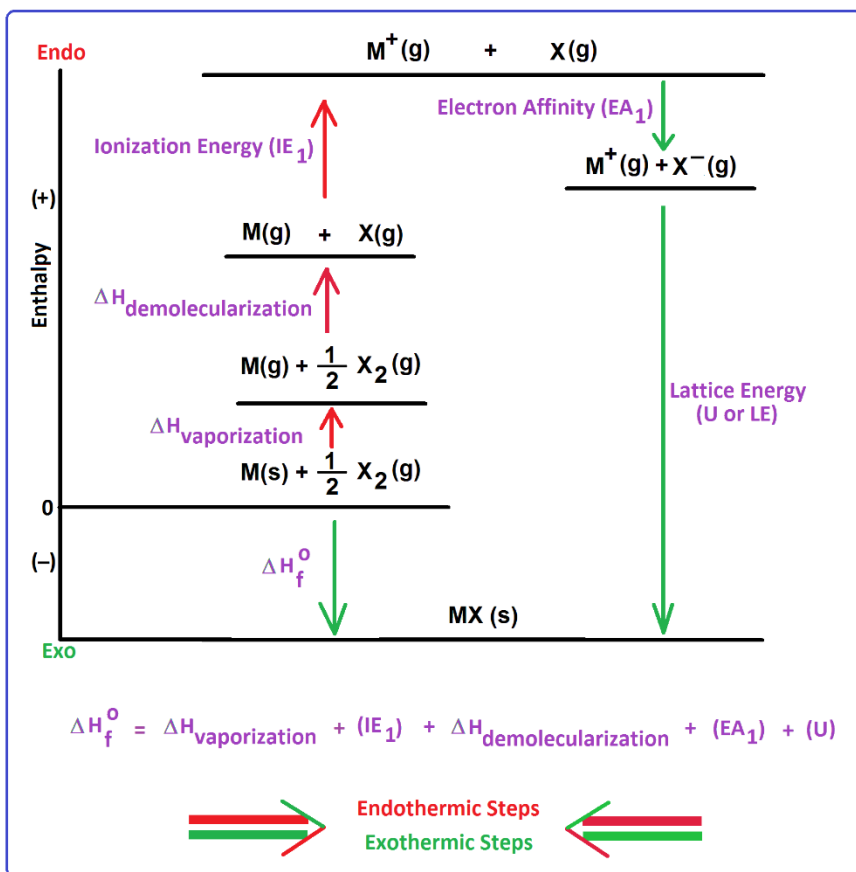
Reaction 3, indicated by the IE_1 , represents the ionization energy necessary to remove the outer electron to form the ionic metal. This step is also endothermic.

Reaction 4, indicated by the EA_1 , is the electron affinity and is the energy necessary for the atomic halogen to “absorb” the additional electron to form ionic halogen. Unlike the previous three steps, this step is exothermic, i.e., it gives off energy.

Reaction 5, indicated by the U or LE, is the lattice energy and allows the two ionic forms to align properly to form the ionic compound. This step is exothermic, as well.

Reaction 6, indicated by the ΔH_f° , is the heat of formation (f) for the overall reaction under standard conditions ($^\circ$) which are 25°C and 1 atmosphere (760 mm Hg) of pressure. ΔH_f° of course, is the change in enthalpy. This reaction is exothermic, too.

Older sources used kcal values for energy; newer texts use kJ for expressing the energy. Either way, remember the conversion: 4.184 kJ = 1 kcal. In this manner, you can easily go back-n-forth between older sources and newer sources.

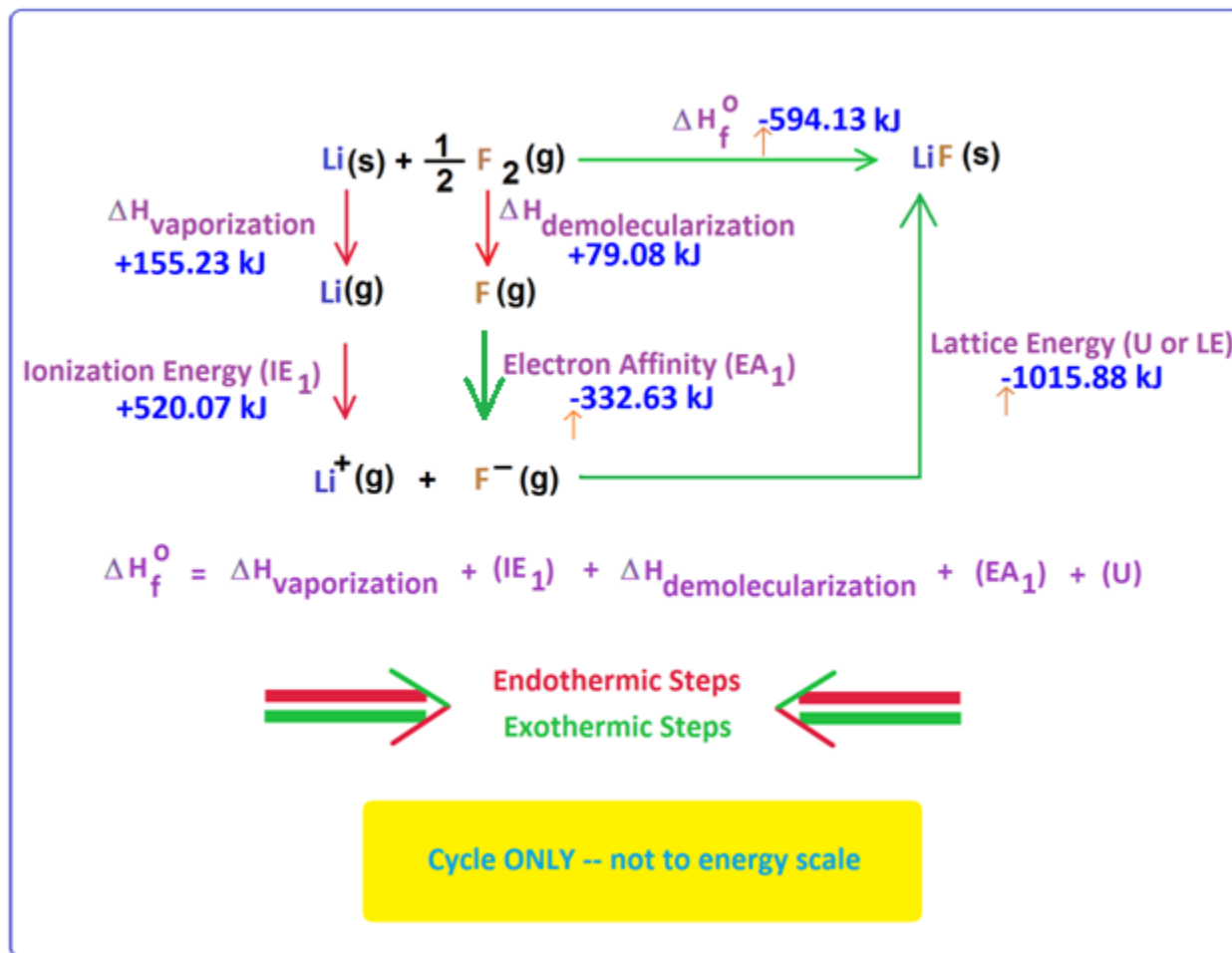


The second method of the Born-Haber Cycle is as above. The difference between this representation and the previous Born-Haber Cycle is that the second Cycle (Born-Haber II) aligns the steps of the reactions along the enthalpy scale (vertical). Color coding remains the same, as do the terms and reactions. The difference, here, is that one sees the relative (not to actual scale) relationship of the energy (endothermic [“endo”] and exothermic [“exo”] in the graphic) to the reaction step.

Applications and Examples

Let's use as our first example to apply Born-Haber the following reaction: $Li(s) + \frac{1}{2}F_2(s) \rightarrow LiF(s)$.

Using the Born-Haber I representation, we obtain the following:



Where each step is as previously (generically) described, i.e.,

Reaction 1, indicated by the $\Delta H_{\text{vaporization}}$, is the energy of vaporization (some authors refer to it as sublimation) of the solid lithium to the gaseous form of the metal. This step is endothermic, i.e., it absorbs energy.

Reaction 2, indicated by the $\Delta H_{\text{demolecularization}}$, is the decomposition of the molecular fluorine to the atomic form (some authors refer to this as dissociation). This step is also endothermic.

Reaction 3, indicated by the IE_1 , represents the ionization energy necessary to remove the outer electron to form the ionic lithium. This step is also endothermic.

Reaction 4, indicated by the EA_1 , is the electron affinity and is the energy necessary for the atomic fluorine to “absorb” the additional electron to form

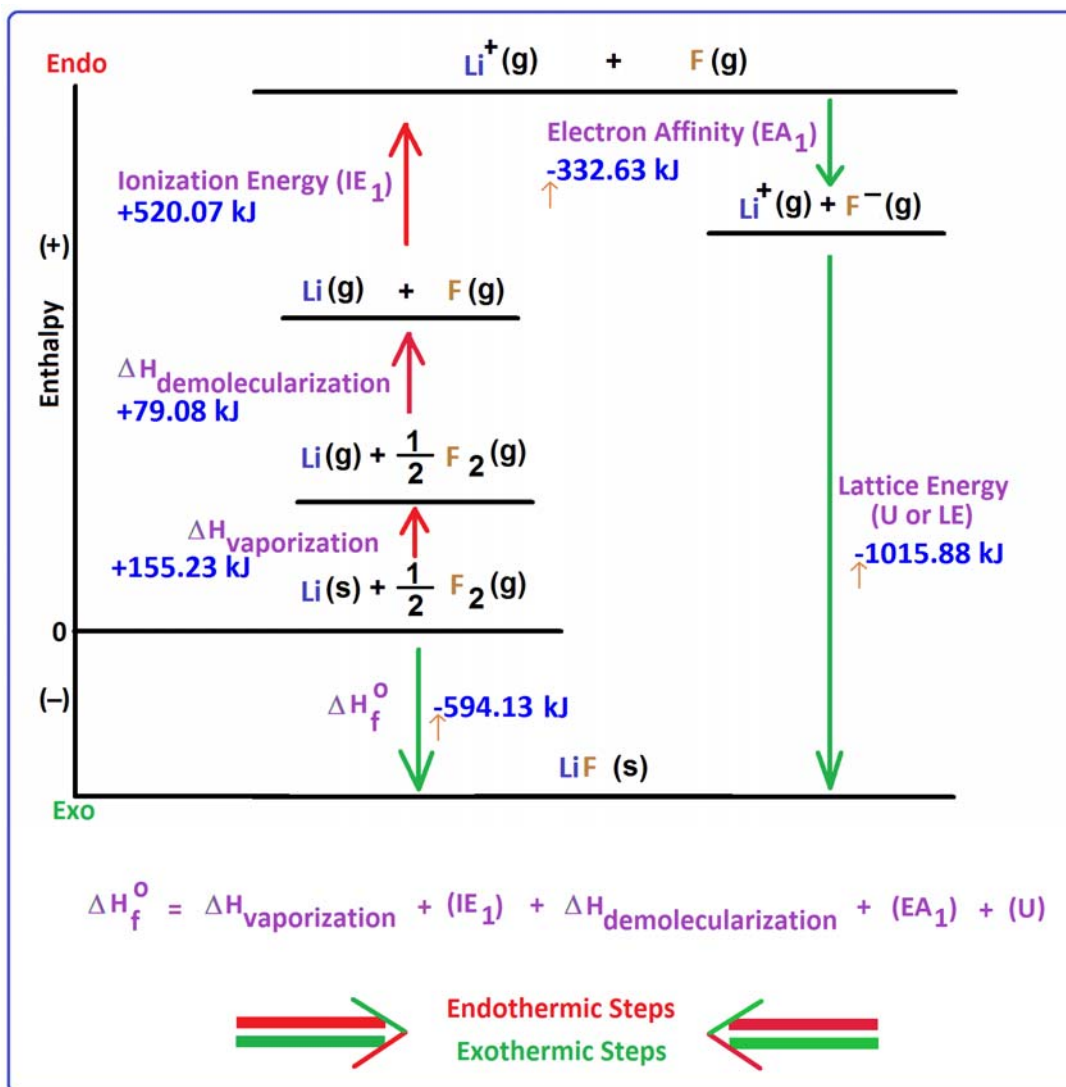
ionic fluorine. Unlike the previous three steps, this step is exothermic, i.e., it gives off energy.

Reaction 5, indicated by the U or LE, is the lattice energy and allows the two ionic forms to align properly to form the ionic compound. This step is exothermic, as well.

Reaction 6, indicated by the ΔH_f° , is the heat of formation ($_f$) for the overall reaction under standard thermodynamic conditions ($^\circ$) which are 25°C and 1 atmosphere (760 mm Hg) of pressure. ΔH , of course, is the change in enthalpy. This reaction is exothermic, too.

Using the Born-Haber II representation (aligning reactions with relative energies) gives us the following:

Note the use of the orange arrows in each graphic to indicate the negative sign.



In each method, the net reaction is exothermic (-); therefore the energy is reduced and the resulting LiF(s) is more thermodynamically stable than Li⁺(g) and the F⁻(g). Occasionally, some authors use the term “bond energy” (or BE) to denote the $\Delta H_{\text{demolecularization}}$. Keep in mind that this BE needs to correspond to the coefficient in front of the halogen. In this case, you only need ½ the energy to overcome the fluorine bonding attractions and this value “is always positive (endothermic)” [5].

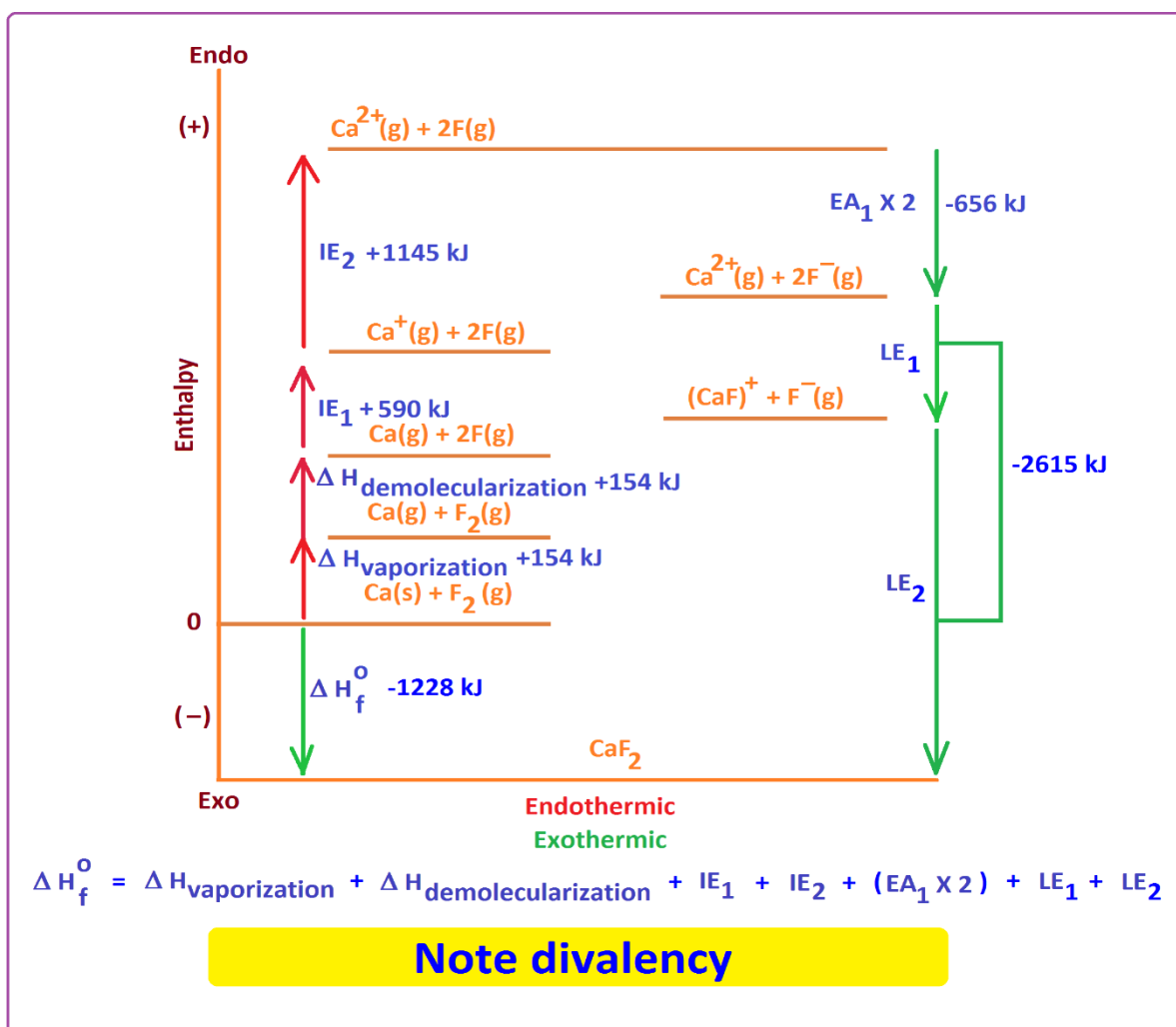
In addition, did you notice that ...

“The ‘up’ direction [in Born-Haber II] is used to indicate endothermic steps in the process, and the ‘down’ direction corresponds to exothermic steps.” [6]?

Good!

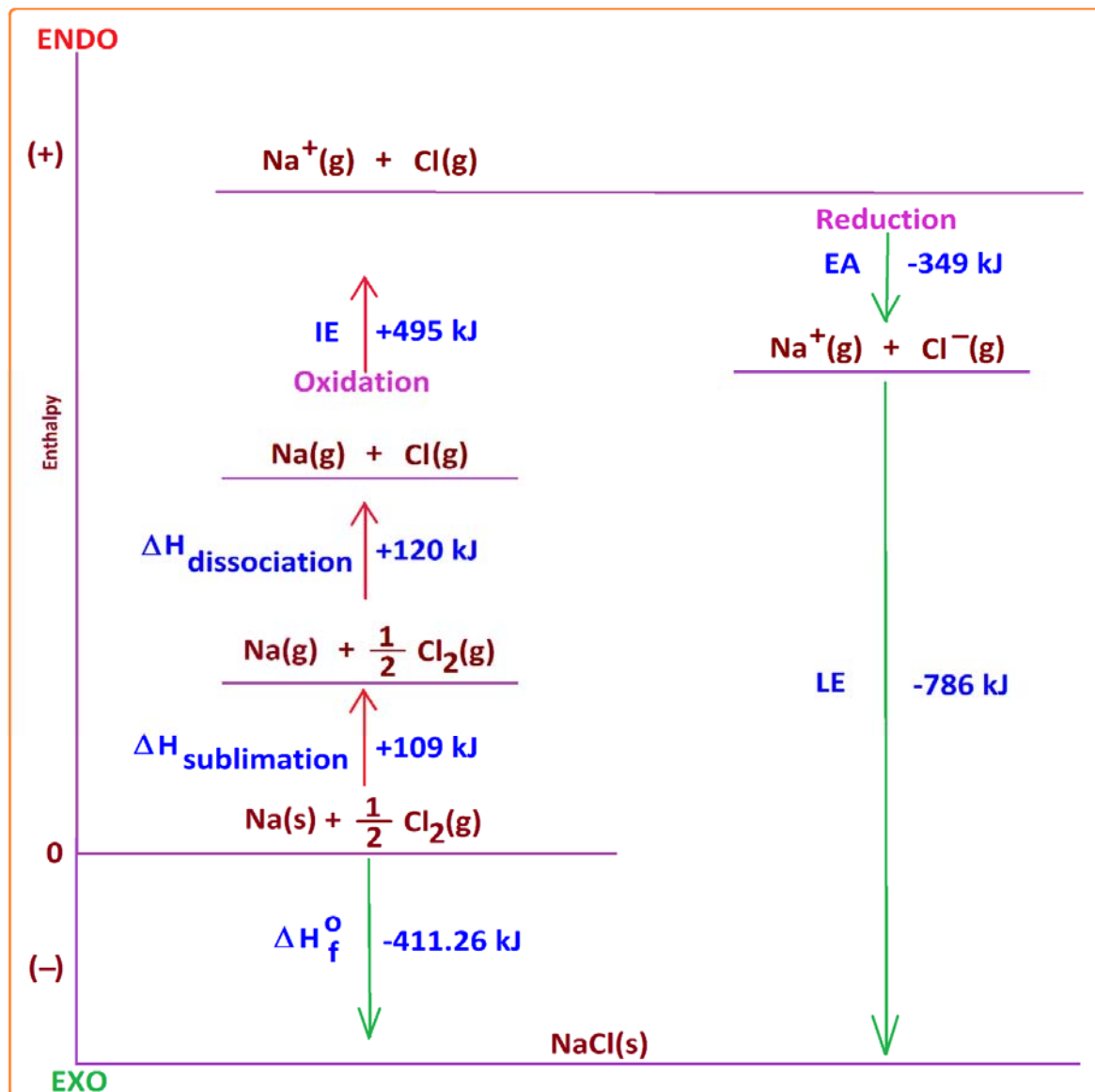
For the remainder of this section, we will focus on Born-Haber II. Do not forget about Born-Haber I, though!

Let’s take a look at a slightly more complex reaction: $\text{Ca(s)} + \text{F}_2(\text{g}) \rightarrow \text{CaF}_2(\text{s})$:



Do you see that there are two (2) ionization energy steps? Good! Calcium, remember, forms a divalent cation when it ionizes. Do you note the sizable difference in the two energies? It takes more energy to remove the second electron than the first. Since the molecular fluorine is dissociated to two atoms, it requires the full bond energy to do so. Lastly, note that because there are two atoms of fluorine, the lattice energy takes two steps to form the final stable compound.

Let's look at one more example using Born-Haber II: $\text{Na(s)} + \frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{NaCl(s)}$.



Did you observe that there is no heat of formation formula with the graphic for NaCl(s) formation? Good! In the space below, show that the heat of formation of NaCl(s) equals the sum of the energies of the different steps:

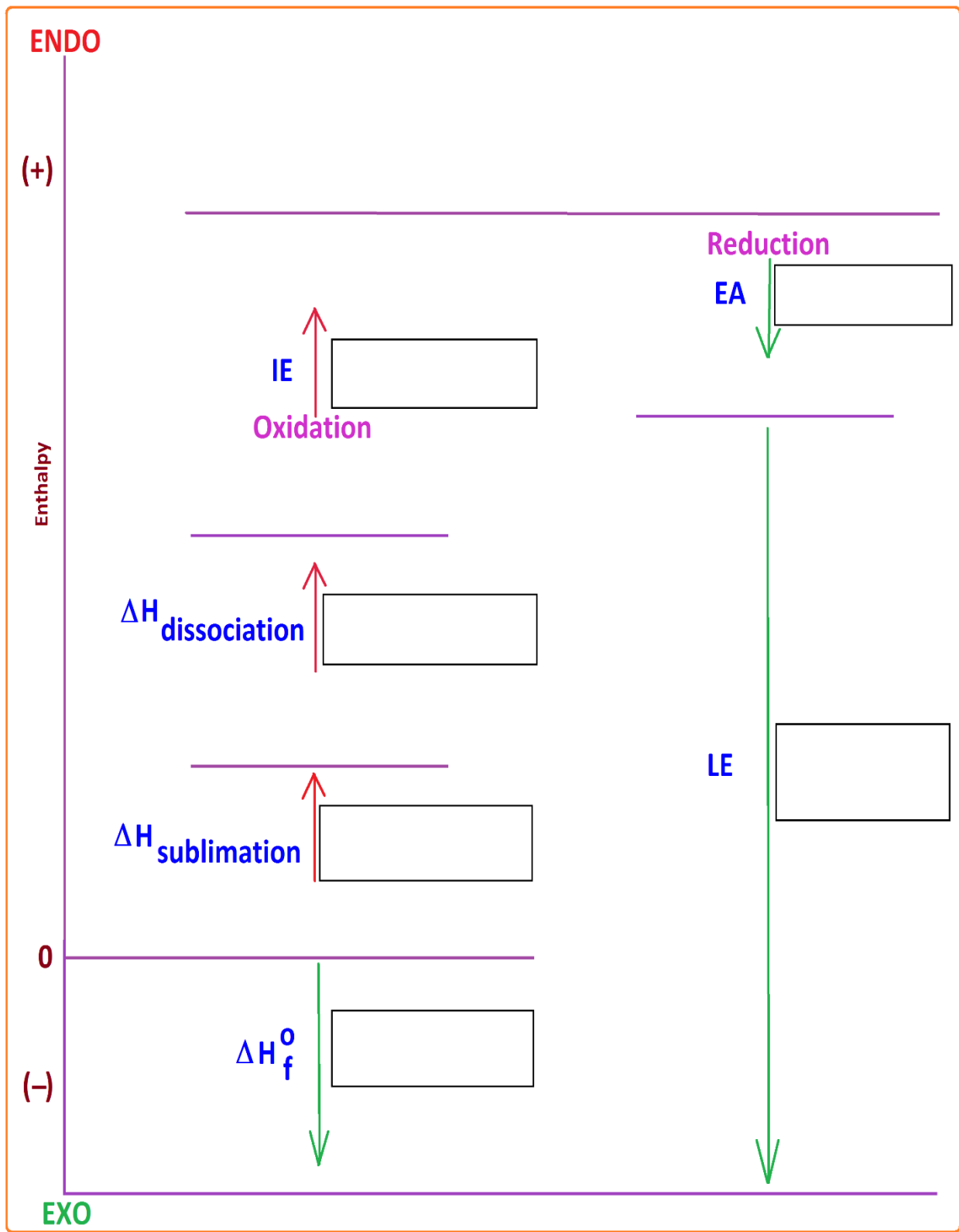
Table of Thermodynamic Values [7 - 11]

Element	$\Delta H_{\text{sublimation}}$ kJ	EA kJ (molecular)	IE kJ	$\Delta H_{\text{demolecularization}}$ kJ (BE; atomic)	Ionic Compound	ΔH°_f kJ	LE kJ calculated
Li	+162		+520		LiF	-612	
Na	+108		+496		LiCl	-409	
K	+90		+419		LiBr	-350	
					LiI	-271	
					NaF	-569	
					NaCl	-411	
F		-328		+79	NaBr	-360	
Cl		-349		+122	NaI	-288	
Br		-325		+112	KF	-562	
I		-295		+107	KCl	-436	
					KBr	-392	
					KI	-328	

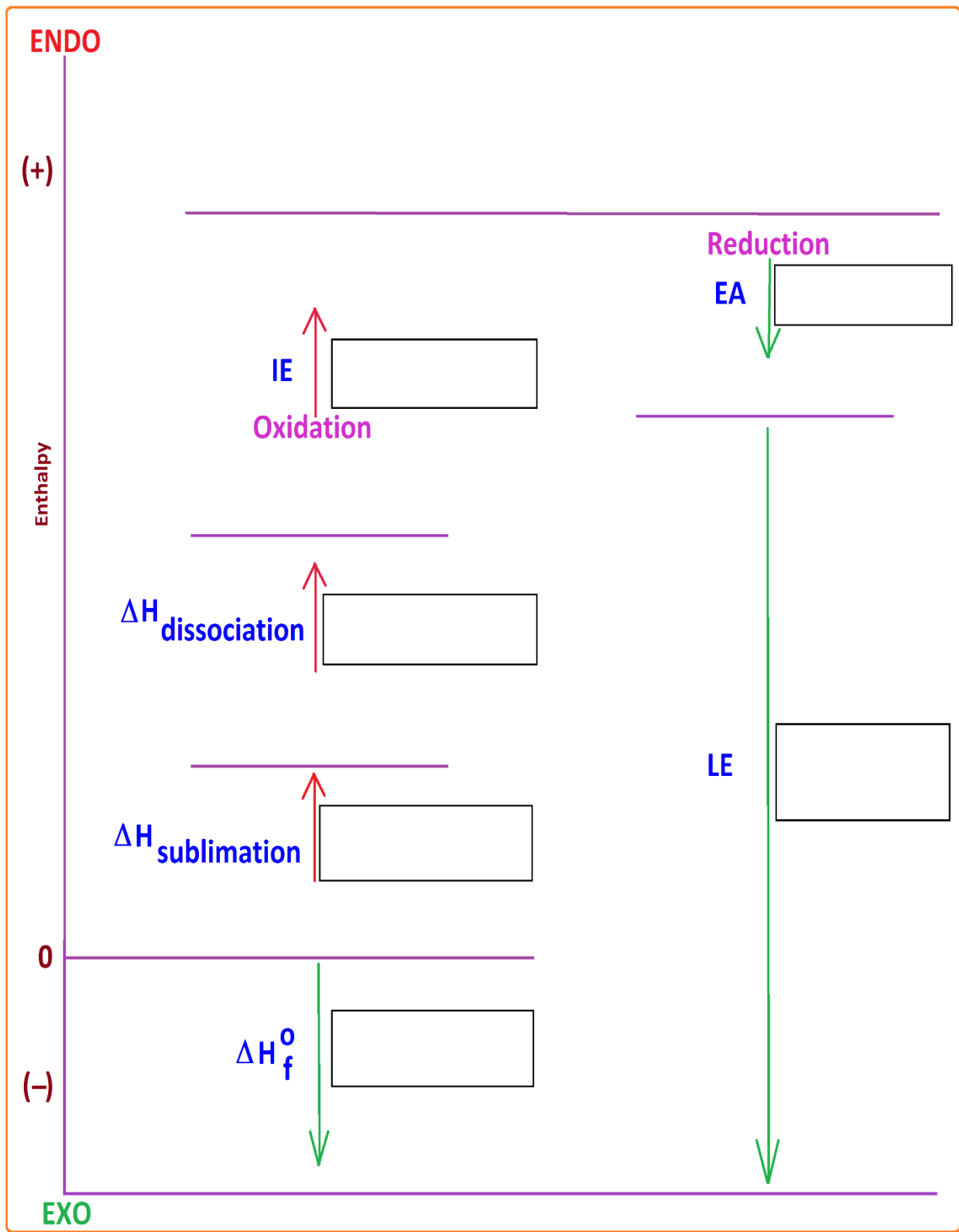
On the following 4 pages, complete the Born-Haber II templates for the formation of four of the ionic compounds above. Calculate the LE's for each reaction. Write the reactions on the purple lines (below), record the appropriate energies in the black boxes (below) and record the LE's for each compound (below in the template) and in the above table.

The completed experiment, including the questions, below, **is due to your lab instructor as you walk into lab to perform the Physiological Thermodynamics experiment in CHEM 121 and as you walk in to perform the experiment in CHEM 122.**

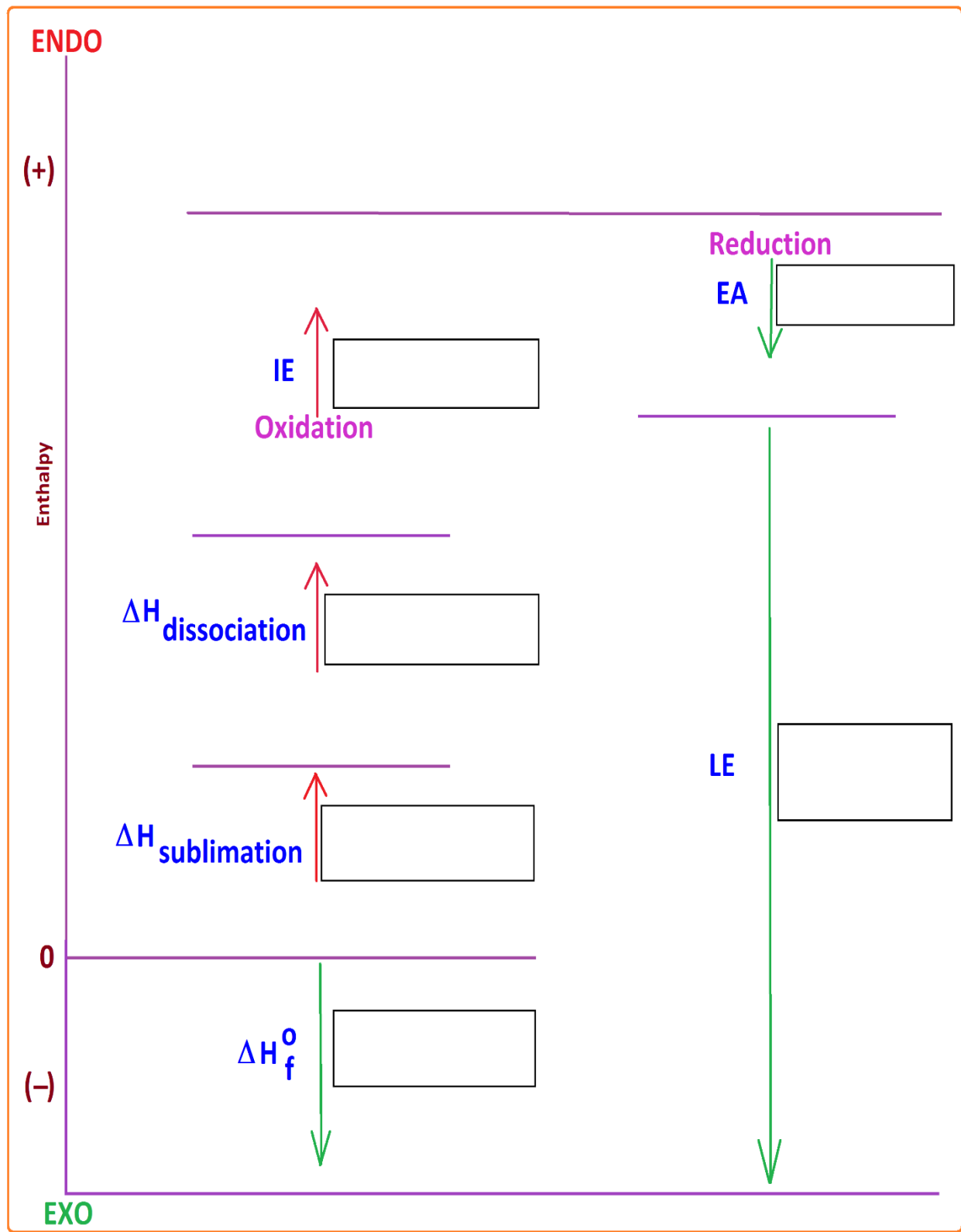
Template 1:



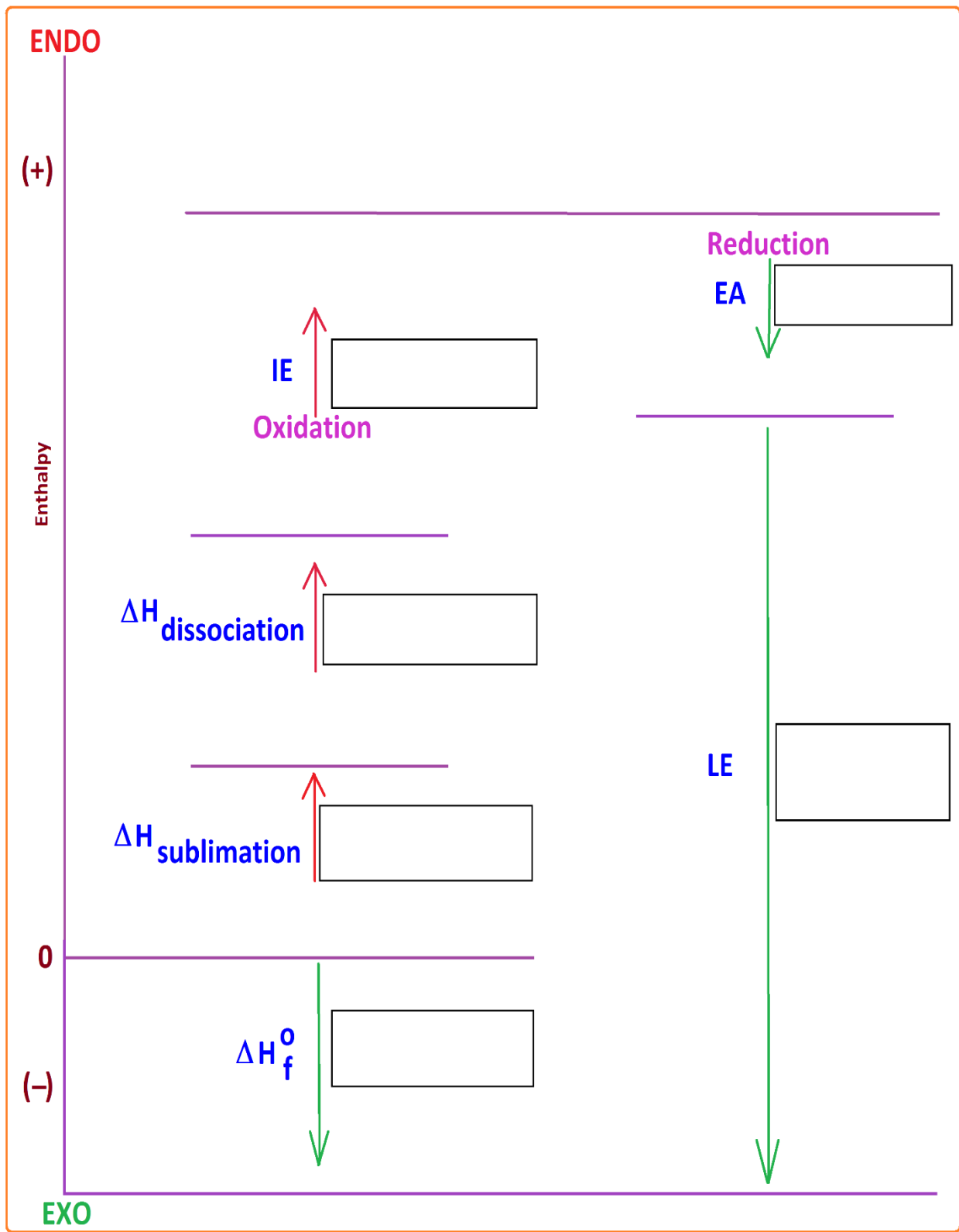
Template 2:



Template 3:



Template 4:



For the remaining 8 ionic compounds, construct your own Born-Haber II diagrams, calculating the LE's (and recording them in the table, above, as well as on your diagram) and arranging the reactions appropriately. Use one page for each Born-Haber II diagram and construct it neatly.

Element or Compound	$\Delta H_{\text{vaporization}}$ kJ	$\Delta H_{\text{dissociation}}$ kJ	IE (total) kJ	EA (total) kJ	$\Delta H_{\text{f}}^{\circ}$ kJ	LE kJ
Mg	+150		+2190			
F (F ₂)		+160		-660		
MgF ₂					-1040	

Grading/Scoring Rubric

Subject	Points possible (middle column for partial credit where due)			Points Earned
	Completely incorrect or no work	Partially Correct	Completely Correct	
Templates pages 11-14	0	6	16	
Hand drawn BH-II, pages 15-22	0	15	48	
Question 1, page 23	0	2	6	
Question 2, page 23	0	2	6	
Question 3, page 23	0		4	
Question 4, pp. 23 and 24	0	10	20	
			Total Points Earned (100 points possible)	

NOTE: This experiment is worth more points than a regular experiment. Plan your work accordingly!

Specific Citations

1. Harvey, K.B. and Porter, G.B.: **Introduction to Physical Organic Chemistry**. (Addison-Wesley Publishing Company, Inc.: Reading, MA) ©1963, p 104.
2. Ibid.
3. King, Edward J.: **Qualitative Analysis and Electrolytic Solutions**. (Harcourt, Brace and World, Inc.: New York) ©1959, p. 86.
4. [http://chemwiki.ucdavis.edu/Physical_Chemistry/Thermodynamics/Thermodynamic Cycles/Hess%27s Law](http://chemwiki.ucdavis.edu/Physical_Chemistry/Thermodynamics/Thermodynamic_Cycles/Hess%27s_Law), Accessed 25 December 2014.
5. Silberberg, M.S.: **Chemistry: The Molecular Nature of Matter and Change**, Second Edition. (McGraw-Hill: Boston) ©2000, p. 342.
6. Rayner-Canham, G. and Overton, T.: **Descriptive Inorganic Chemistry**, Fourth Edition. (W. H. Freeman and Company: New York) ©2006, p. 116.
7. <http://chemistry.bd.psu.edu/jircitano/ionize.html>, Accessed 25 December 2014.
8. <http://chemistry.bd.psu.edu/jircitano/affinity.html>, Accessed 25 December 2014.
9. <http://chemistry.bd.psu.edu/jircitano/sublime.html>, Accessed 25 December 2014.
10. <http://chemistry.bd.psu.edu/jircitano/diss.html>, Accessed 25 December 2014.
11. <http://chemistry.bd.psu.edu/jircitano/format.html>, Accessed 25 December 2014.

General References

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