Lattice Energy and the Born-Haber Cycle

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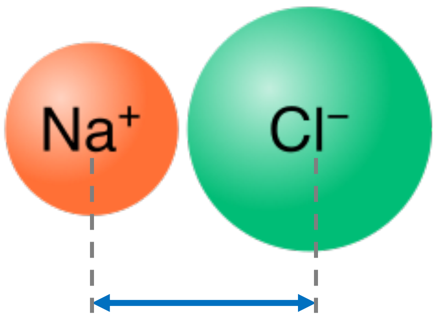
Strength of Ion-Ion Interactions

The strength of ion-ion interactions is dependent on two things:

1. Charges of the ions: q_1 & q_2
2. Radii of ions or distance between them: d

$$E \propto \frac{q_1 \times q_2}{d}$$



For NaCl:

- $q_1 = +1$ (charge on cation)
- $q_2 = -1$ (charge on anion)
- $d = r(Na^+) + r(Cl^-)$

Quantifying the Strength of Ion-Ion Interactions: Lattice Energy (U)

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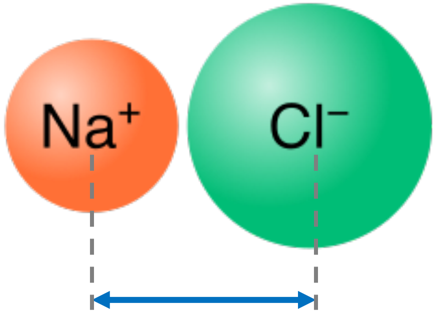

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- $q_1 = +1$ (charge on cation)
- $q_2 = -1$ (charge on anion)
- $d = r(Na^+) + r(Cl^-)$

$$U = k\frac{q_1 \times q_2}{d}$$

To go from the proportionality expression (gray equation with ∝) to an equivalence expression (red equation with =), we need a proportionality constant (k).

WHAT IS LATTICE ENERGY?

It is the enthalpy change for the following process:

$$M^{m+}\,(g) + N^{n-}\,(g) \rightarrow M_nN_m\,(s)$$

Where 1 mole of an ionic compound (M_nN_m) forms from its free ions in the gas phase (M^{m+} and N^{n-}).

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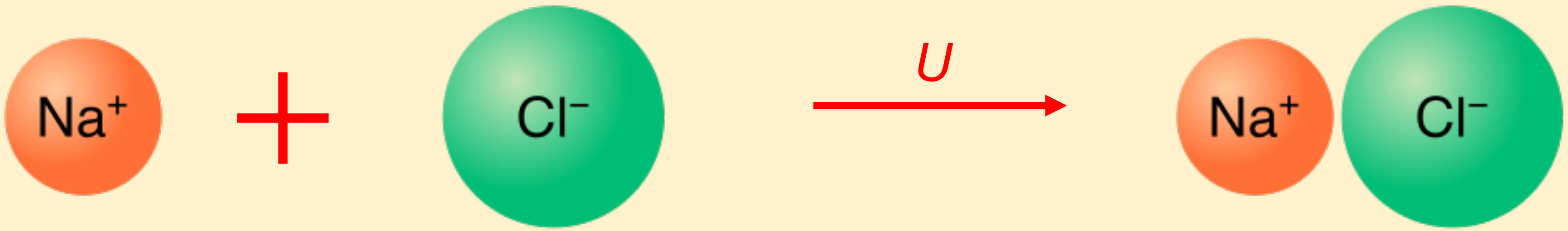
For example, the lattice energy for NaCl (s) corresponds to this process:

$$Na^{+}\ (g) + Cl^{-}\ (g) \rightarrow NaCl\ (s)$$



How to calculate lattice energy (U) of $CaCl_2$?

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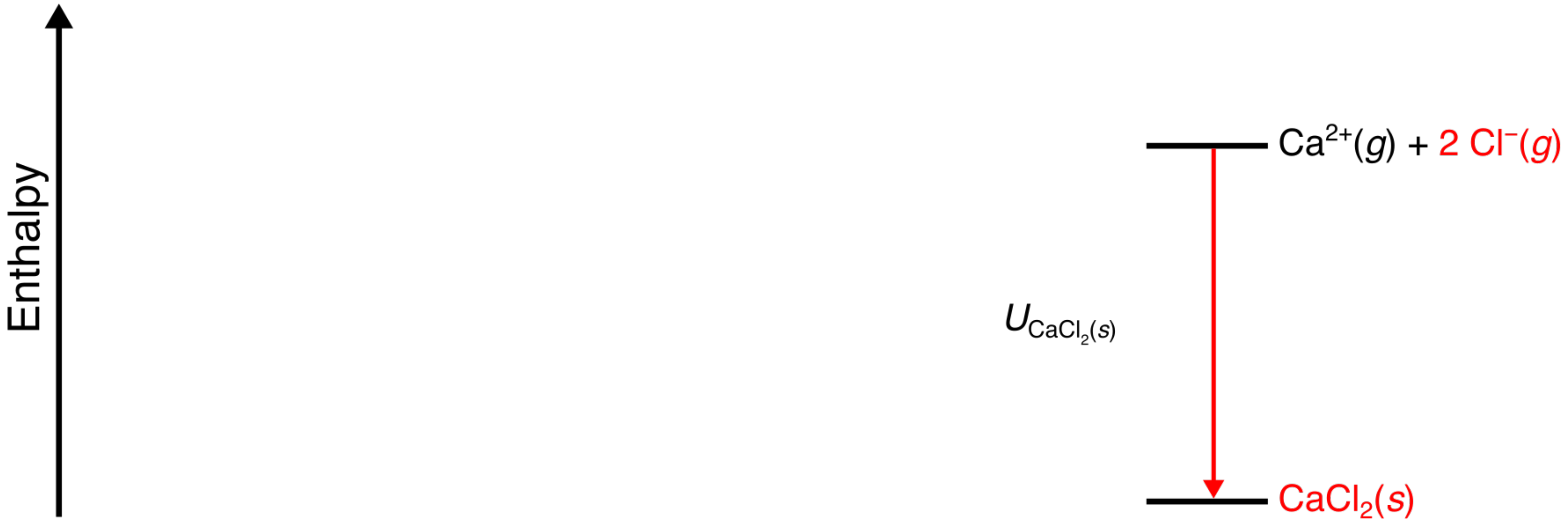
Hint: Try to use the definition of lattice energy and Hess's Law.

This is the definition of lattice energy (U).



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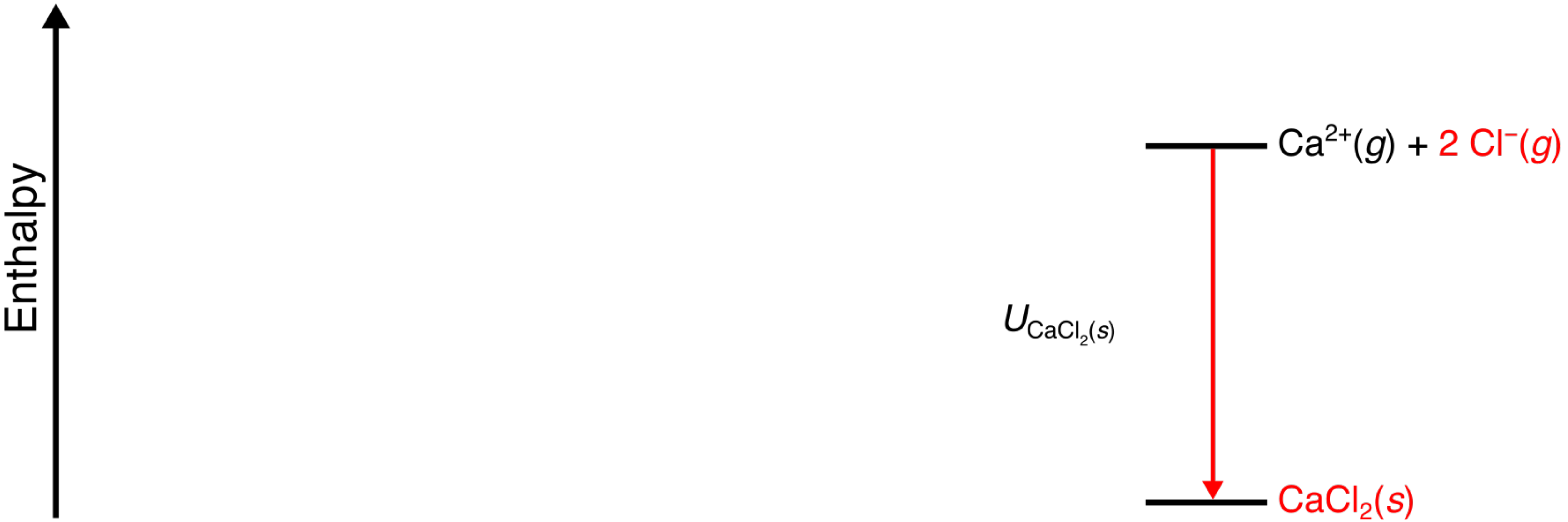
Now how do I get to these free ions?



How to calculate lattice energy (U) of $CaCl_2$?

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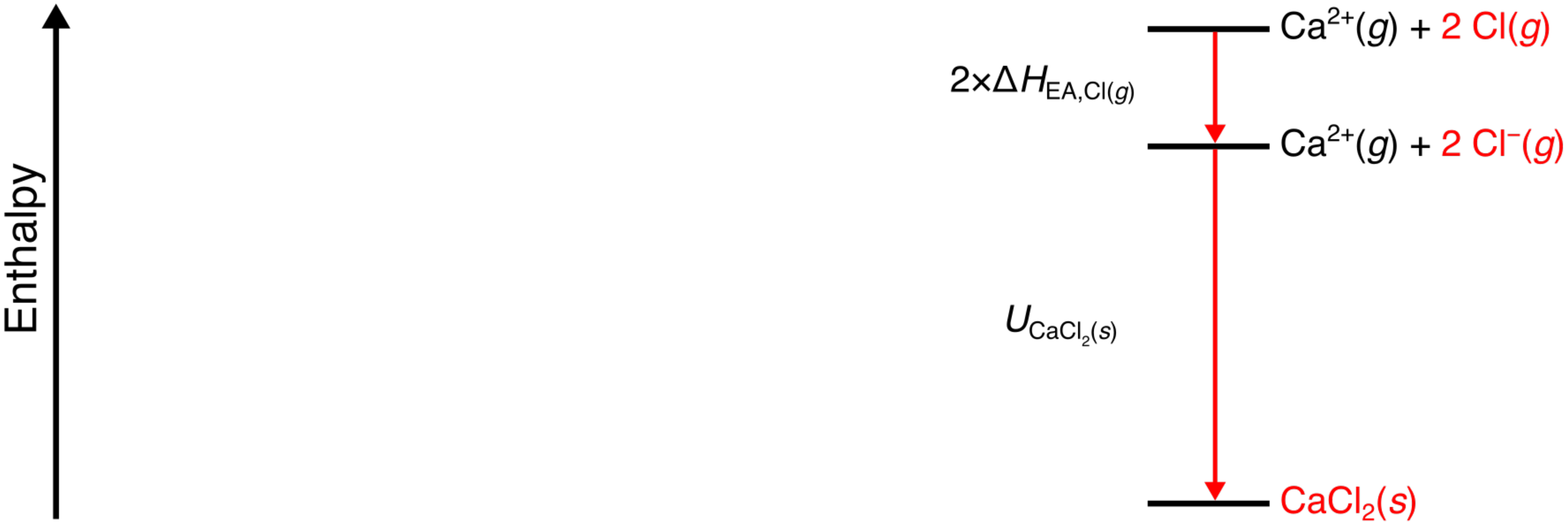
Now how do I get to these free ions? I can get Cl^- (g) by electron affinity!



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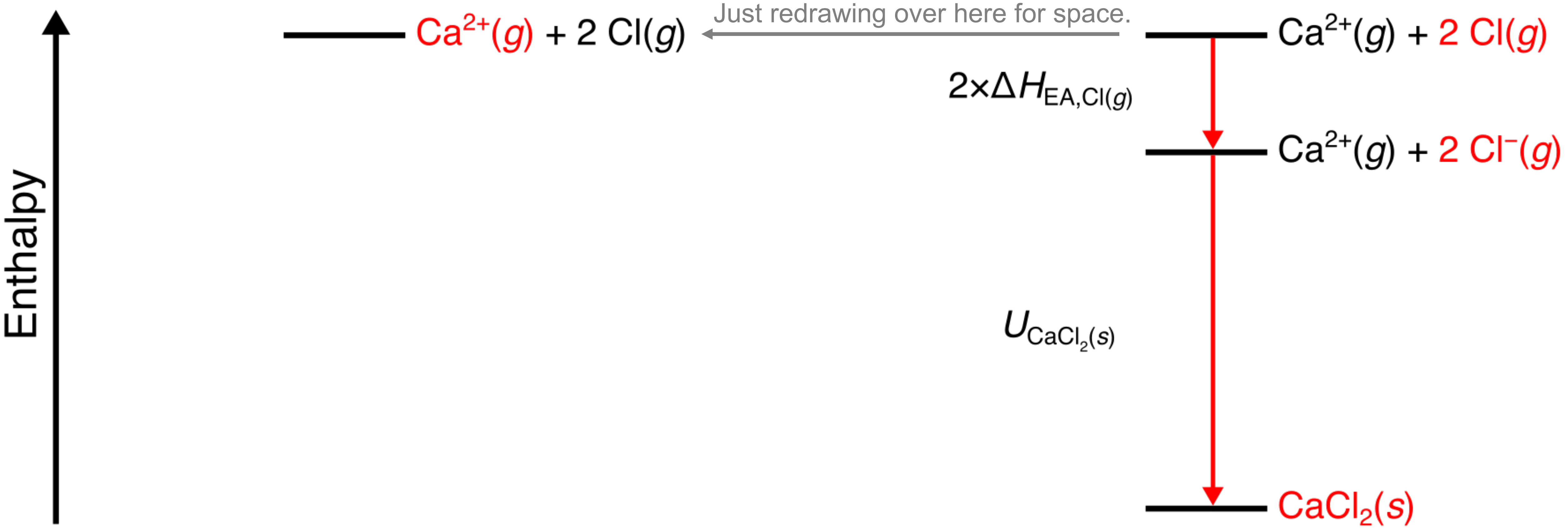
Hint: Try to use the definition of lattice energy and Hess's Law.

How about Ca^{2+} (g)?



How to calculate lattice energy (U) of $CaCl_2$?

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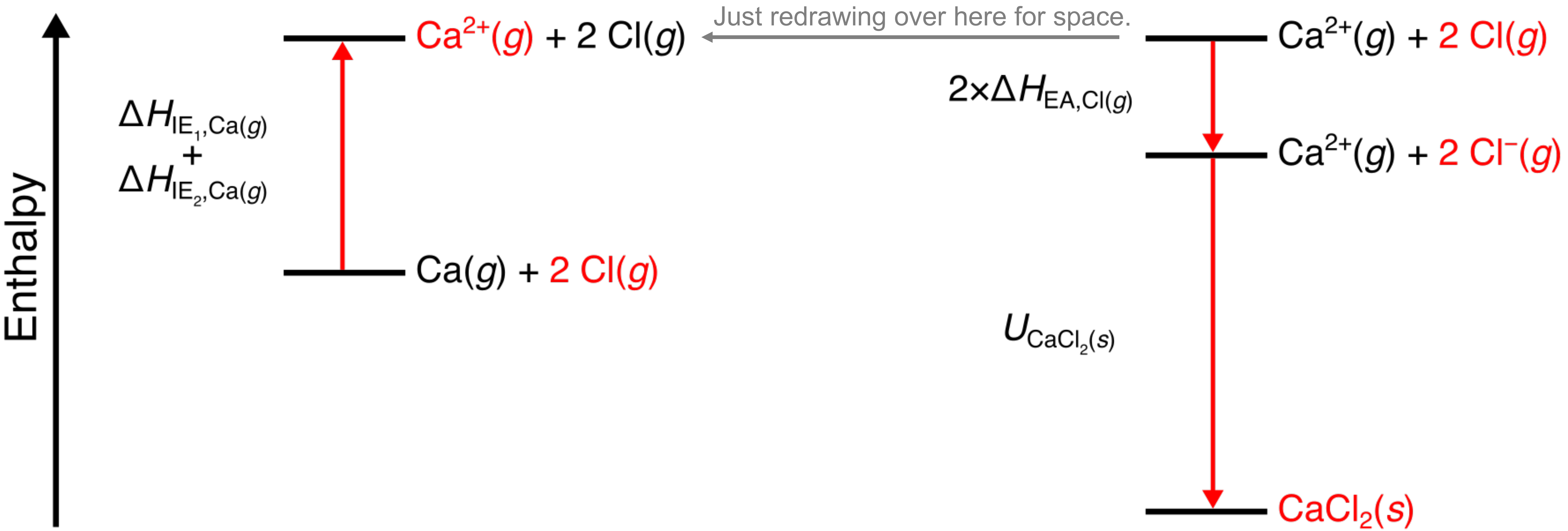
How about Ca^{2+}? I can get Ca^{2+} from ionizing Ca (g) twice!



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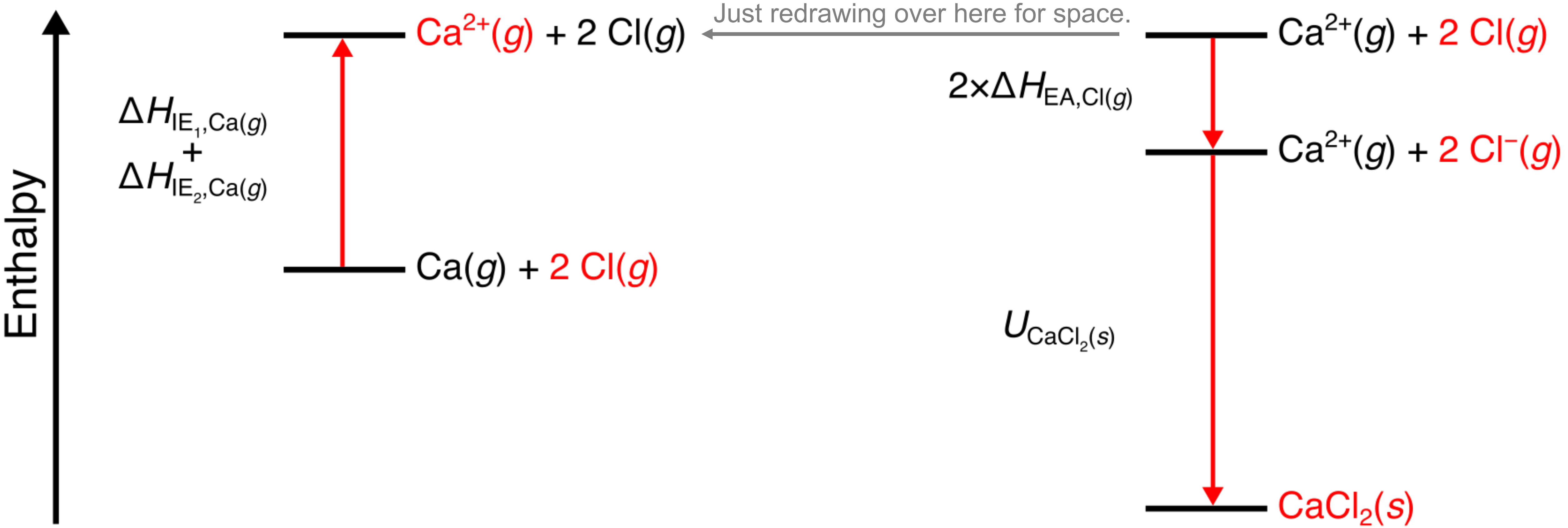
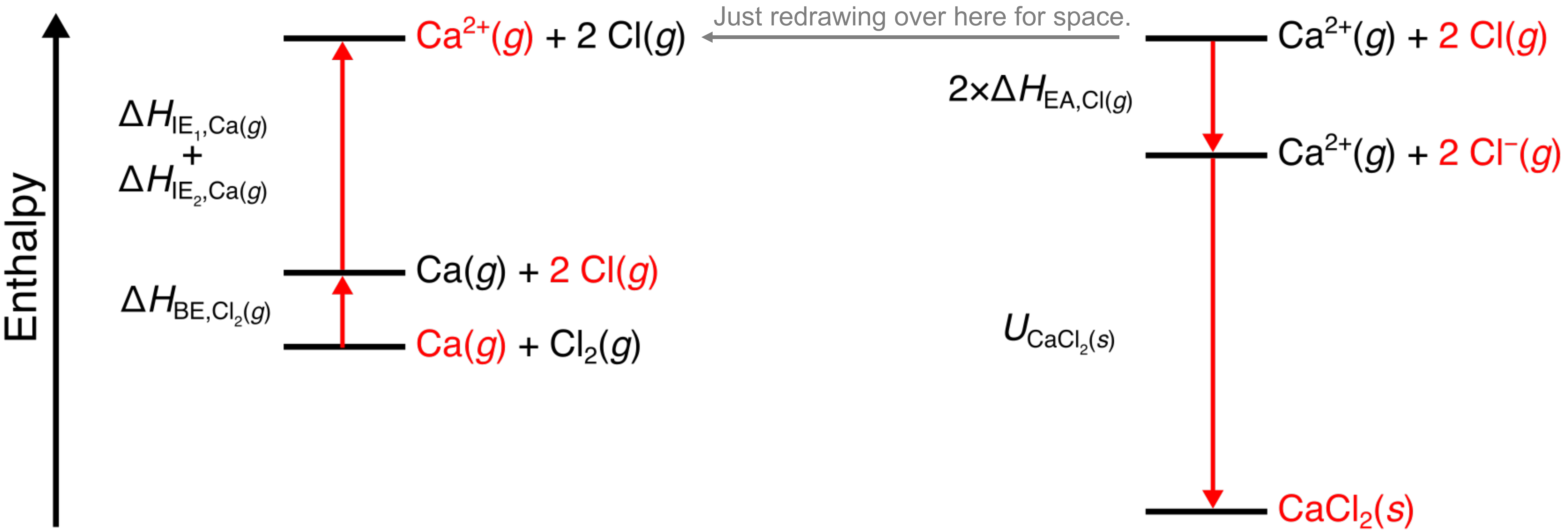
How do I get Cl (g)?



How to calculate lattice energy (U) of $CaCl_2$?

Hint: Try to use the definition of lattice energy and Hess's Law.

How do I get Cl (g)? By breaking apart Cl_2 (g)!



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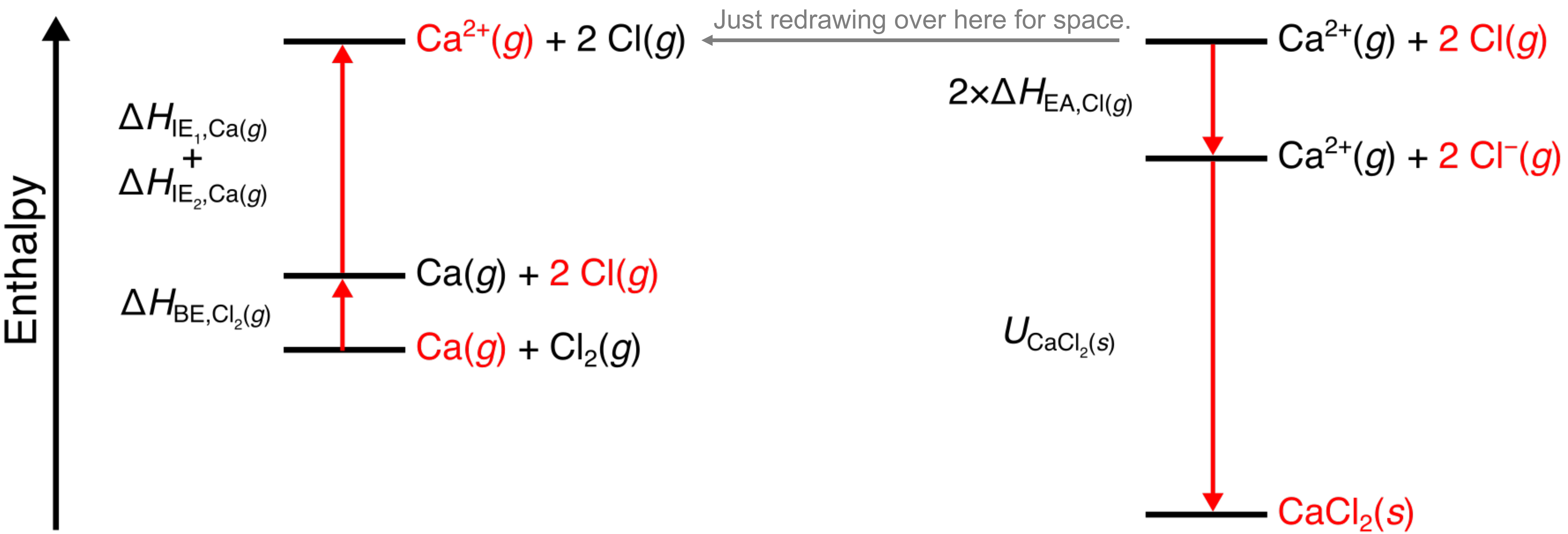
How do I get Ca (g)?



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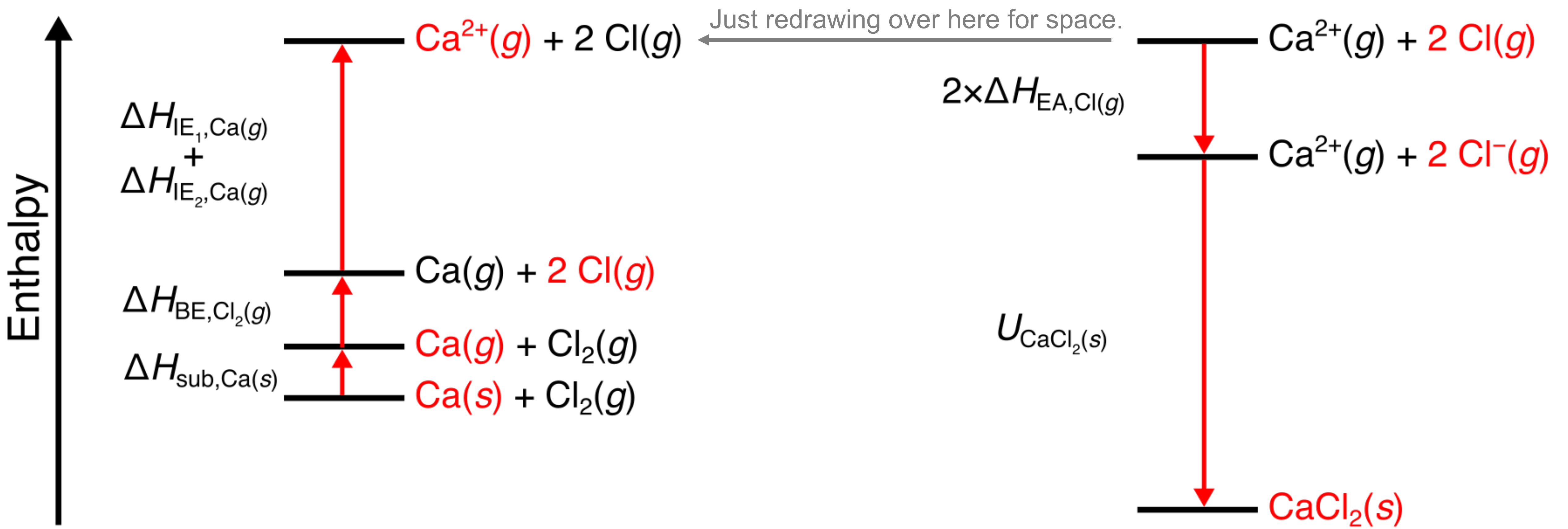
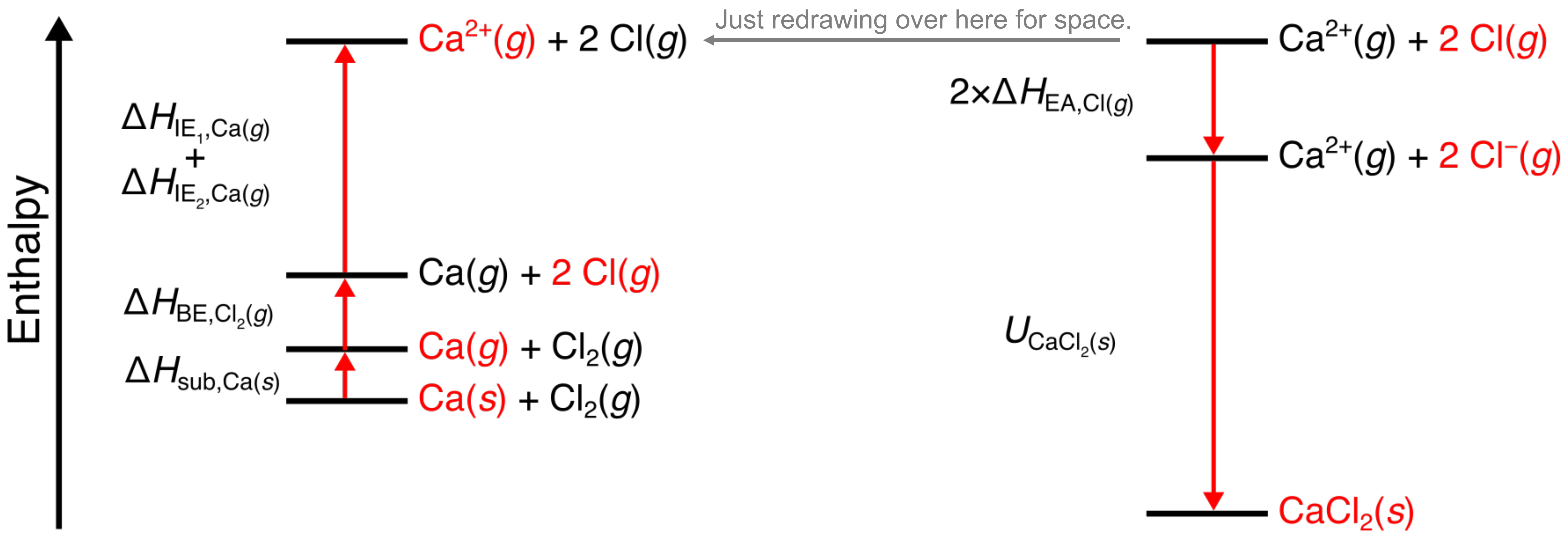
How do I get Ca (g)? By subliming Ca (s)!



How to calculate lattice energy (U) of $CaCl_2$?

Hint: Try to use the definition of lattice energy and Hess's Law.

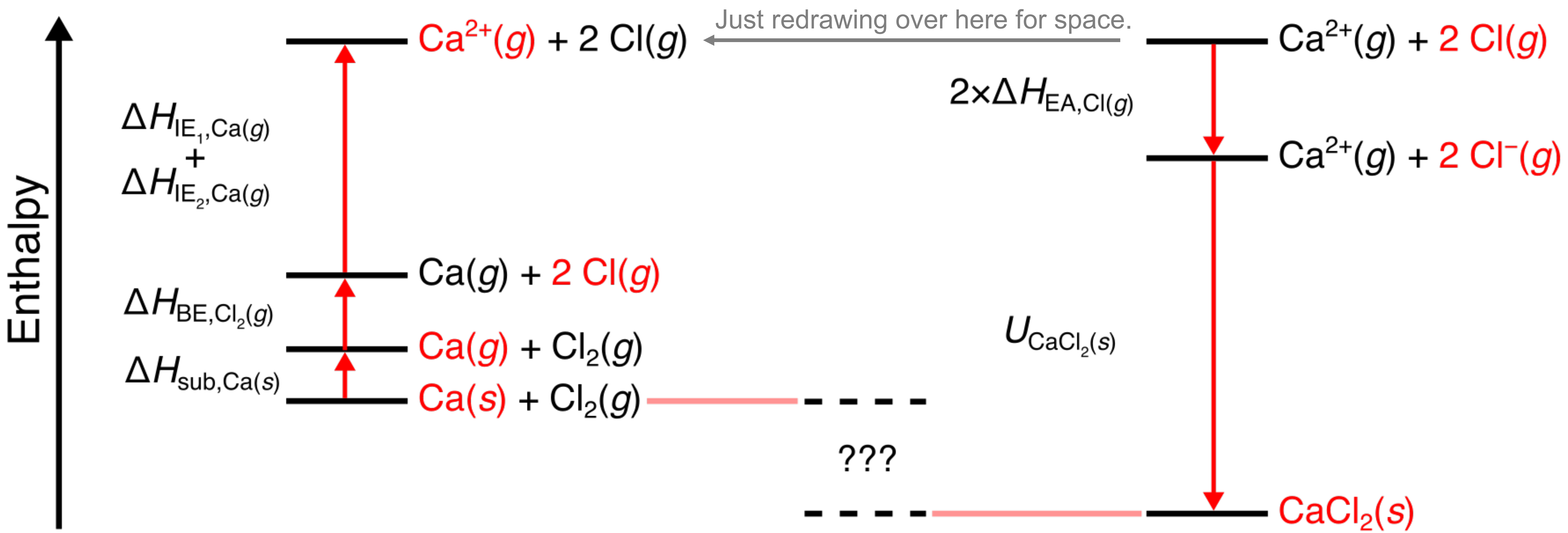
The up processes are endothermic. The down processes are exothermic.



How to calculate lattice energy (U) of $CaCl_2$?

Hint: Try to use the definition of lattice energy and Hess's Law.

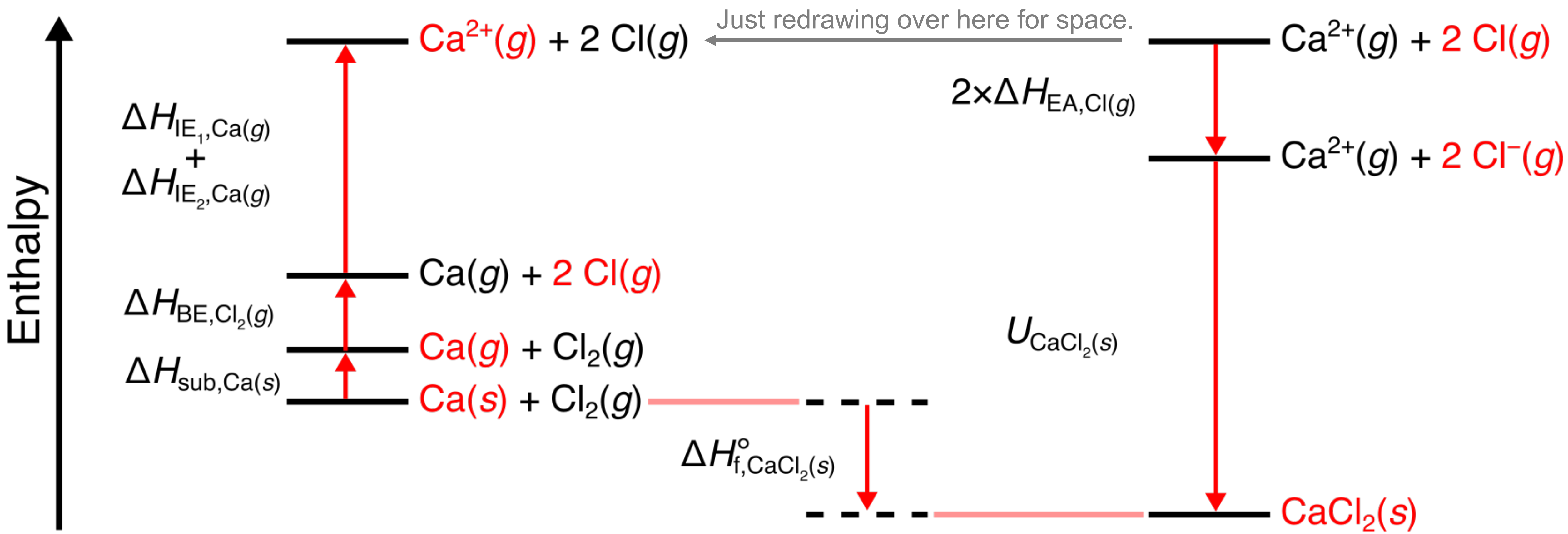
Now how do I connect Ca (s) + Cl_2 (g) to $CaCl_2$ (s)?



How to calculate lattice energy (U) of $CaCl_2$?

Hint: Try to use the definition of lattice energy and Hess's Law.

Now how do I connect Ca (s) + Cl_2 (g) to $CaCl_2$ (s)? Heat of formation!



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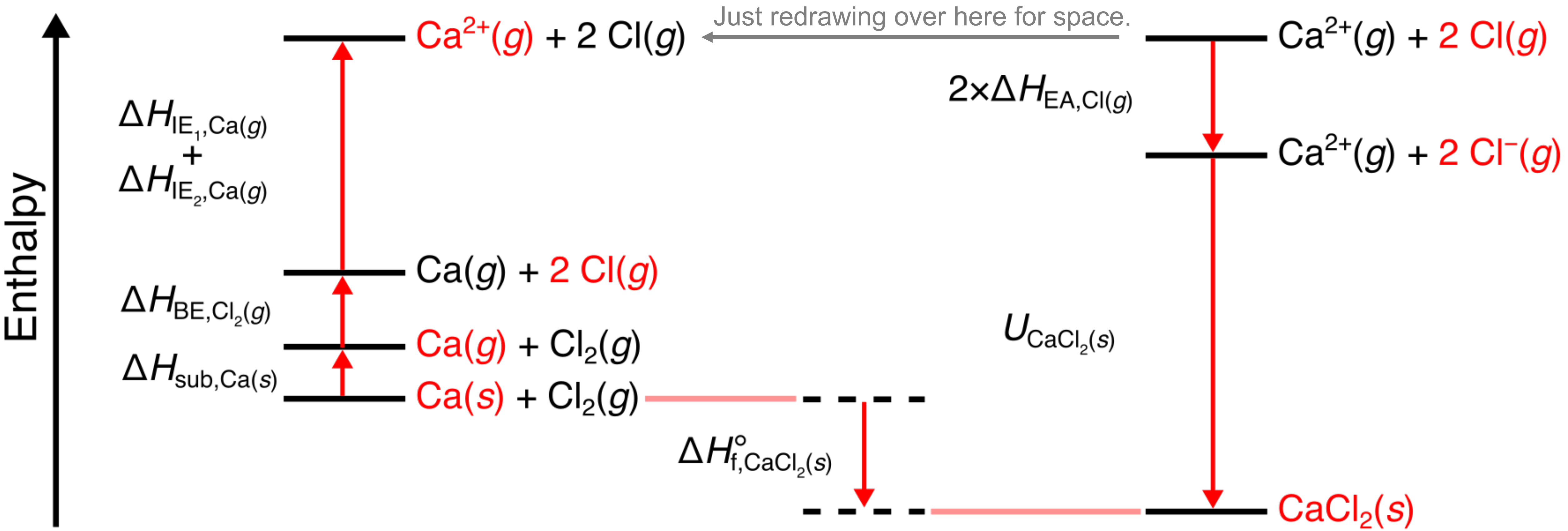
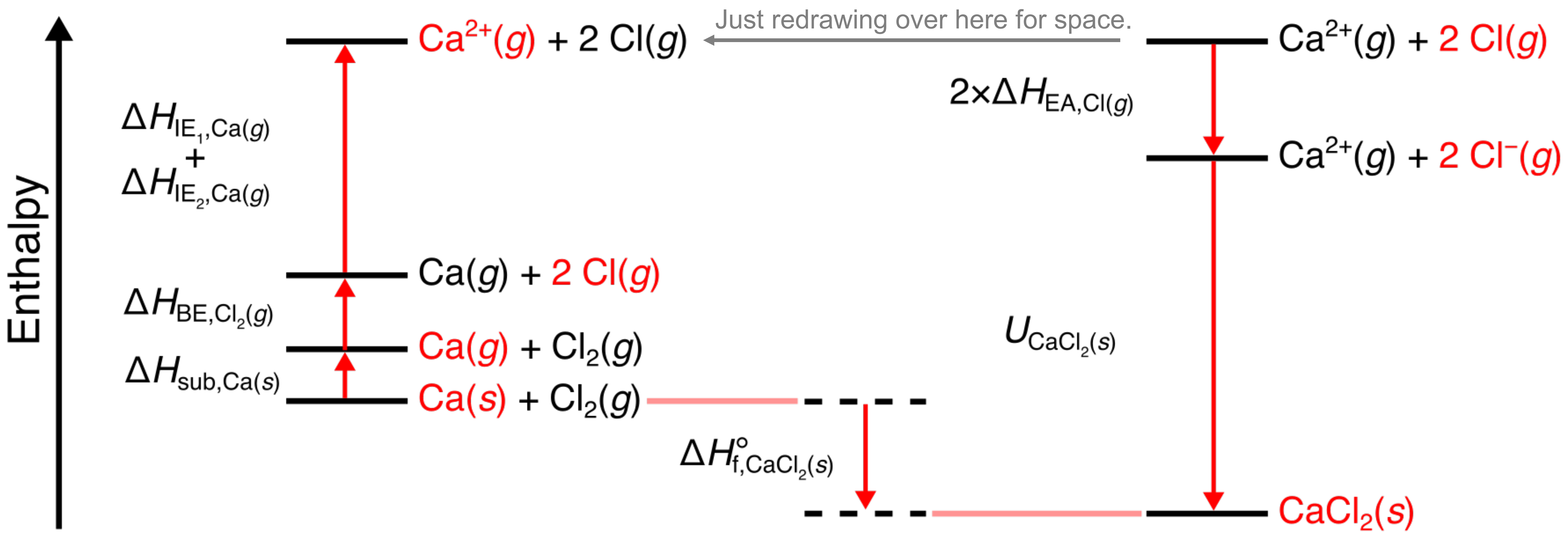
By Hess's Law, we know we can then express the heat of formation as the sum of all these processes:



How to calculate lattice energy (U) of $CaCl_2$?

By Hess's Law, we know we can then express the heat of formation as the sum of all these processes:

$$\Delta H_f^o = \Delta H_{sub} + \Delta H_{BE} + (\Delta H_{IE1} + \Delta H_{IE2}) + 2\times\Delta H_{EA} + U$$



Calculate the lattice energy (U) of $CaCl_2$?

Without going back to the previous slides can you actually solve for lattice energy if given:

$$\Delta H_f^o\,[\mathrm{CaCl_2}\,(s)] = -795.4\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{sub}}\,[\mathrm{Ca}\,(s)] = 154\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{BE}}\,[\mathrm{Cl_2}\,(g)] = 240\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta H_{\mathrm{IE1}}[\mathrm{Ca}\,(g)] = 590\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{IE2}}[\mathrm{Ca}\,(g)] = 1145\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{EA}}\,[\mathrm{Cl}\,(g)] = -349\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

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$$\Delta H_f^o = \Delta H_{\mathrm{sub}} + \Delta H_{\mathrm{BE}} + (\Delta H_{\mathrm{IE1}} + \Delta H_{\mathrm{IE2}}) + 2\times\Delta H_{\mathrm{EA}} + U$$

$$-795.4\,\frac{\mathrm{kJ}}{\mathrm{mol}} = 154\,\frac{\mathrm{kJ}}{\mathrm{mol}} + 240\,\frac{\mathrm{kJ}}{\mathrm{mol}} + \left(590\,\frac{\mathrm{kJ}}{\mathrm{mol}} + 1145\,\frac{\mathrm{kJ}}{\mathrm{mol}}\right) + 2\times\left(-349\,\frac{\mathrm{kJ}}{\mathrm{mol}}\right) + U$$

$$U = -2226\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Calculate the lattice energy (U) of Na_2O.

$$\Delta H_f^o\,[\mathrm{Na_2O}\,(s)] = -416\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{sub}}\,[\mathrm{Na}\,(s)] = 109\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{BE}}\,[\mathrm{O_2}\,(g)] = 499\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta H_{\mathrm{IE1}}[\mathrm{Na}\,(g)] = 495\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{EA1}}[\mathrm{O}\,(g)] = -141\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad \Delta H_{\mathrm{EA2}}\,[\mathrm{O}\,(g)] = 744\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Hint: Be careful with stoichiometry here!

Calculate the lattice energy (U) of Na_2O.

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$$\Delta H_{IE1}[Na\,(g)] = 495\,\frac{kJ}{mol} \quad \Delta H_{EA1}[O\,(g)] = -141\,\frac{kJ}{mol} \quad \Delta H_{EA2}\,[O\,(g)] = 744\,\frac{kJ}{mol}$$

$$\Delta H_f^o = 2\times\Delta H_{sub} + \frac{1}{2}\times\Delta H_{BE} + 2\times\Delta H_{IE1} + (\Delta H_{EA1} + \Delta H_{EA1}) + U$$

$$-416\,\frac{kJ}{mol} = 2\times\left(109\,\frac{kJ}{mol}\right) + \frac{1}{2}\times\left(499\,\frac{kJ}{mol}\right) + 2\times\left(495\,\frac{kJ}{mol}\right) + \left(-141\,\frac{kJ}{mol} + 744\,\frac{kJ}{mol}\right) + +U$$

$$U = -2477\,\frac{kJ}{mol}$$

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