LATTICE ENERGY

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Definition and Symbol

- The energy given off when oppositely charged ions in the gas phase come together to form a solid.
- Symbol = U_o
- Signed by (-)

- The greater lattice energy:
  - Cation-anion distance <<<
  - Ions charge >>>

Determinations

- Born-Lande equation
  - Crystal structure are known
- Kapustinskii equation
  - Crystal structure are not known
- Born-Haber Cycles
  - Based on Hess Law

Born-Lande Equation

$$U_o = \frac{N.Z^{+}.Z^{-}.M.e^2}{4\pi\varepsilon_o r_o} x \left(1 - \frac{1}{n}\right)$$

$$U_o = \frac{N.e^2}{4\pi\varepsilon_o} x \frac{M.Z^{+}.Z^{-}}{r_o} x \left(1 - \frac{1}{n}\right)$$

- N = Avogadro number = 6.02×10^{23}
- Z^{+} = positive charge
- Z^{-} = negative charge
- M = Madelung constant
- e^{-} = electron charge = 1.6021×10^{-19}C

- π = 3.14159
- ε_o = dielectric contants of a vacuum

  = $8.854 \times 10^{-12} C^2 m^{-1} J^{-1}$
- n = factor for compressibility
- r_o = cation-anion equilibrium distance

  = $r_+ + r_-$

Madelung Constant

Lattice	M
Rock salt	1.7476
CsCl	1.7627
Zinc blende	1.6381
Fluorite	2.5194

Compressibility factor

Element	n
He	5
Ne	7
Ar, Cu	9
Kr, Ag	10
Xe, Au	12

$$\left.\begin{array}{l} {}_{11}Na^{+} = [{}_{10}Ne] \rightarrow n = 7 \\ {}_{17}Cl^{-} = [{}_{18}Ar] \rightarrow n = 9 \end{array}\right\} n = \frac{7+9}{2} = 8$$

- Substituting the constants, yields:

$$U_o = 1.390x10^{-4} \text{ x } \frac{M.Z^{+}.Z^{-}}{r_o} \text{ x } \left(1 - \frac{1}{n}\right)$$

Kapustinskii Equation

$$U_o = \frac{120200\,\nu . Z^{+} . Z^{-}}{r_o} \times \left(1 - \frac{34.5}{r_o}\right)$$

ν = number of ions per molecule

ν NaCl = 2

Z^{+} = positive charge

Z^{-} = negative charge

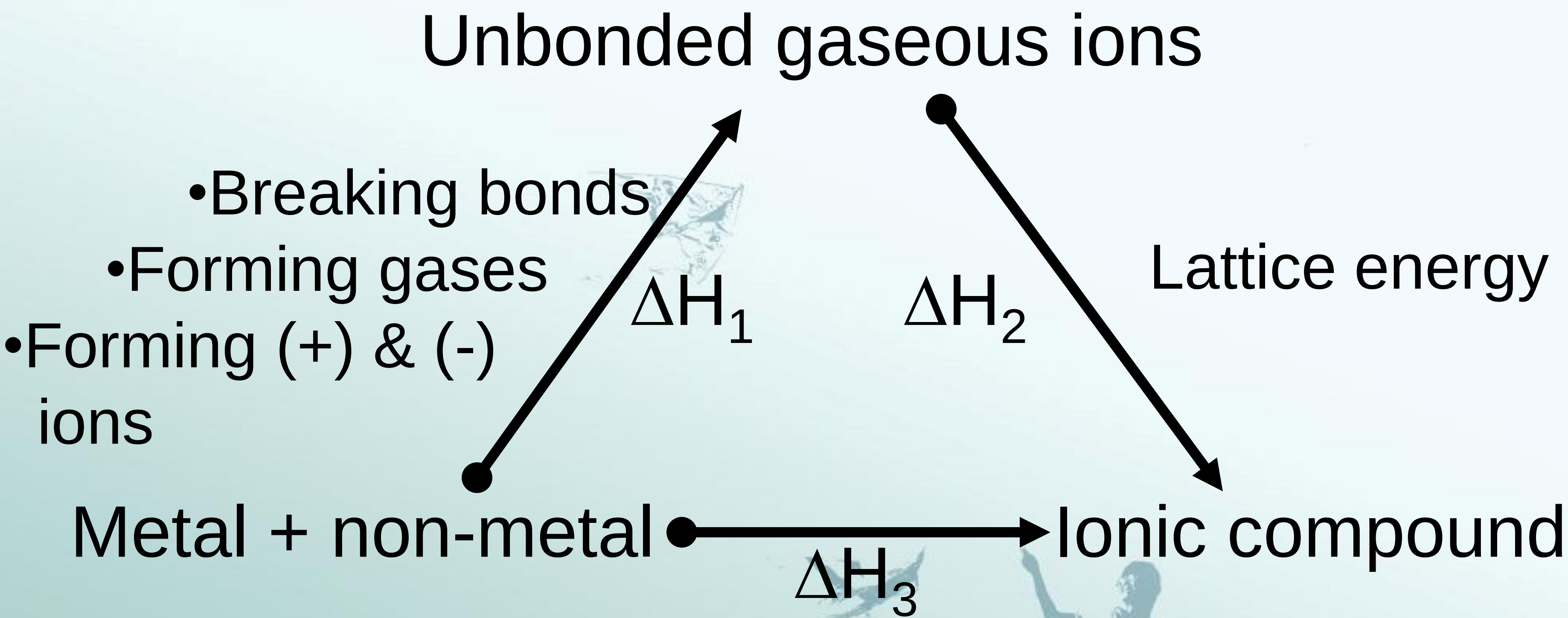
r_o = cation-anion equilibrium distance

= $r_{+} + r_{-}$

Comparison

- Lattice energy of NaCl
  - Experiment = -755 $kJ.mol^{-1}$
  - Born-Lande = -770 $kJ.mol^{-1}$
  - Kapustinskii = -753 $kJ.mol^{-1}$

Born Haber Cycle



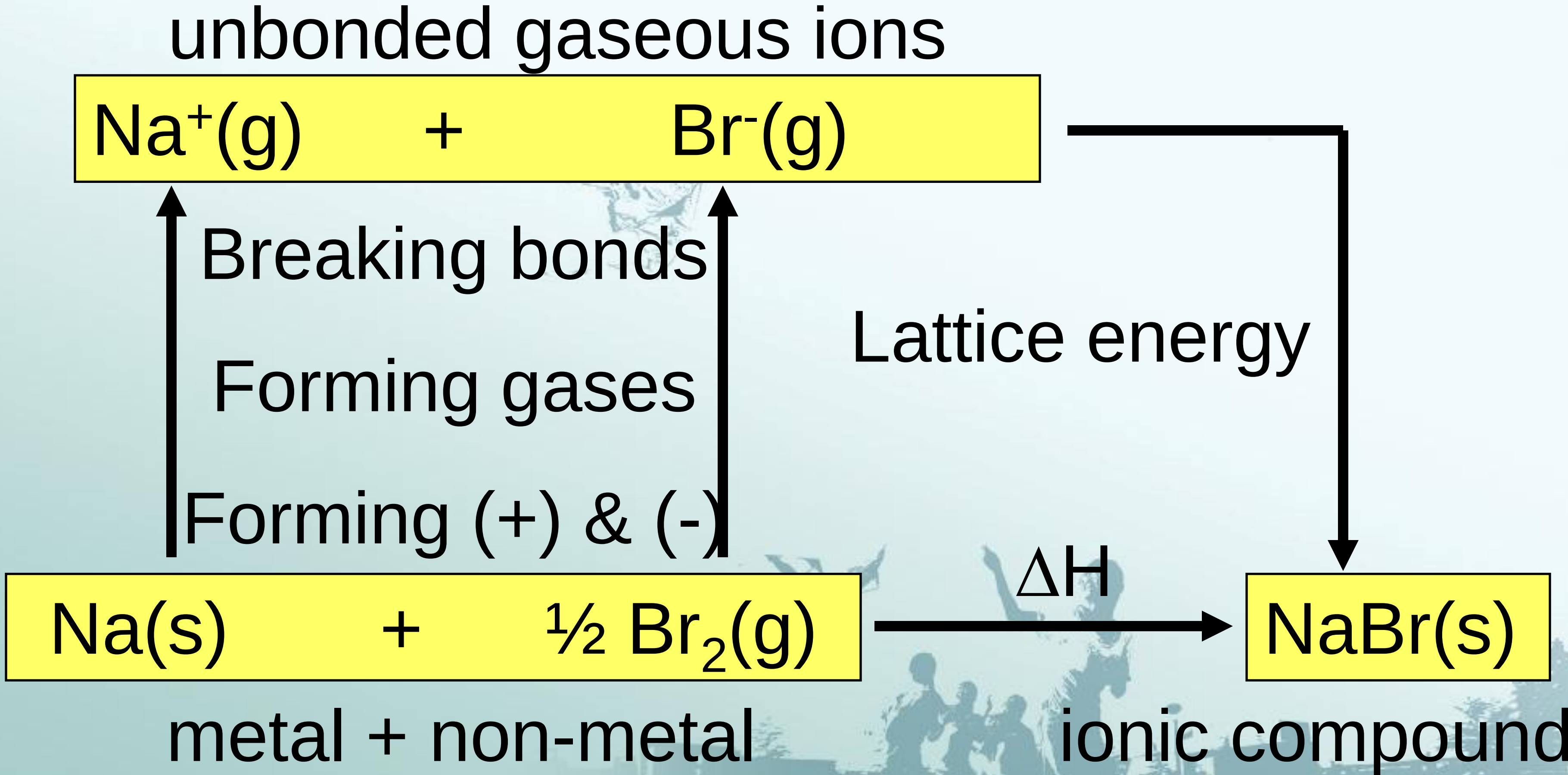
$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

Example

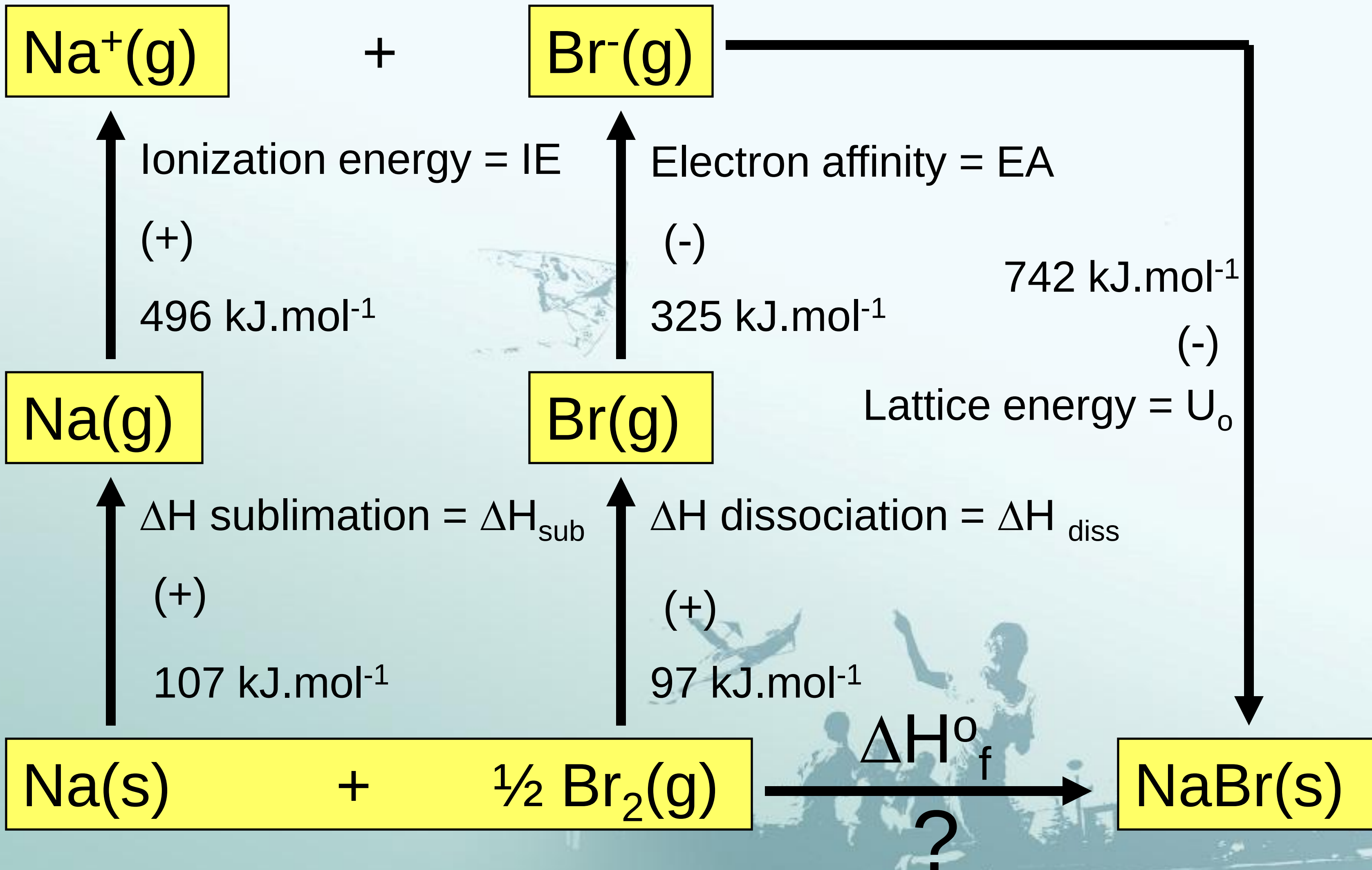
Problem 1:

Sketch the born-haber cycles and calculate the enthalpy formation of sodium bromide: $Na(s) + \frac{1}{2} Br_2(g) \rightarrow NaBr(s)$

- $\Delta H_{sublimation}$ (Na) = 107 $kJ.mol^{-1}$
- $\Delta H_{dissociation}$ (Br) = 194 $kJ.mol^{-1}$
- Ionization energy (Na) = 496 $kJ.mol^{-1}$
- Electron affinity (Br) = -325 $kJ.mol^{-1}$
- Lattice energy (NaBr) = -742 $kJ.mol^{-1}$


unbonded gaseous ions
$Na^+(g)$ + $Br^-(g)$
Breaking bonds
Forming gases
Forming (+) & (-)
Lattice energy
ΔH
Na(s) + ½ $Br_2(g)$
NaBr(s)
metal + non-metal
ionic compound

Breaking down each of the stages



The enthalpy formation of NaBr:

ΔH^o_f NaBr

$=[(\Delta H_{sub} + IE)_{Na} + (\Delta H_{diss} + (-EA)_{Br}] + (-U_o)_{NaBr}$

$= (\Delta H_{sub} + IE)_{Na} + (\Delta H_{diss} - EA)_{Br} - (U_o)_{NaBr}$

$= 107 + 496 + 97 - 325 - 742$

$= -367$ kJ.mol^{-1}

The more stable compound

- Why sodium chloride is NaCl not $NaCl_2$?

	NaCl	$NaCl_2$
IE_1	+496 $kJ.mol^{-1}$	+496 $kJ.mol^{-1}$
IE_2		+4562 $kJ.mol^{-1}$
U_o	-787 $kJ.mol^{-1}$	-2155 $kJ.mol^{-1}$
ΔH^o_f	-441 $kJ.mol^{-1}$	+2555 $kJ.mol^{-1}$

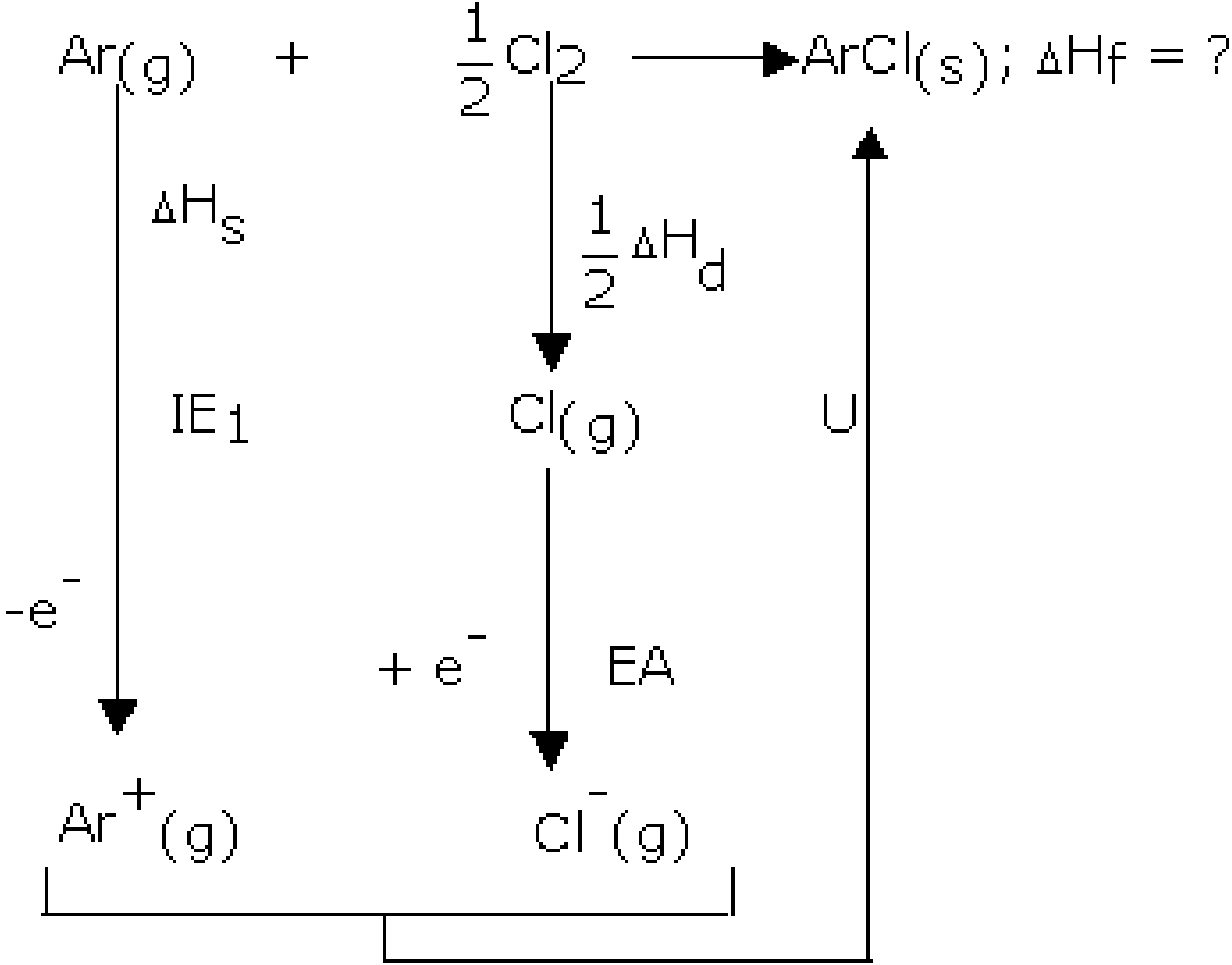
- NaCl
  - The lattice energy can compensate the first ionization energy
  - The enthalpy formation is negative
  - Stable

- $NaCl_2$
  - The lattice energy can not compensate the first and second ionization energy
  - The enthalpy formation is positive
  - Unstable

- Problem 2:
- Predict the stability of the ArCl molecule, from the reaction:

$$Ar(g) + \frac{1}{2} Cl_2(g) \rightarrow ArCl\ (s)$$

- if:
  - Δ_H dissociation of Cl_2 = 243 $kJ.mol^{-1}$
  - Electron Affinity of Cl^- = -349 $kJ.mol^{-1}$
  - 1-st IE of Ar = 1526.3 $kJ.mol^{-1}$
  - Uo of ArCl(s) = -703 $kJ.mol^{-1}$


Ar(g) + 1/2 Cl2 → ArCl(s); ΔHf = ?
ΔHs
1/2 ΔHd
IE1
-e-
Cl(g)
U
+ e-
EA
Ar+(g)
Cl-(g)

$$\Delta H_f = IE_1 + \frac{1}{2}\Delta H_d + EA + U = 1526.3 + \frac{1}{2}(243) - 349.0 - 703$$

$$= 595.5 \text{ kJ mol}^{-1}$$

The + value of ΔH^o_f indicates that net energy is required for this process. Hence, formation ArCl is energetically unfavourable.

Problem 3

- The 1-st, 2-nd and 3-rd ionization energy and sublimation energy of Q are 390, 765, 3012 and 160 respectively (kJ/mol). The dissociation energy of O_2 and the entalphy formation O^{2-} ion are 206 and 1097 (kJ/mol).
- Lattice energy is determined by

$$Uo = \frac{n \cdot z^{+} \cdot z^{-}}{r_o}\left(1 - \frac{34.5}{r_o}\right)K$$

- If $K = 1.21 \times 10^5$ kJ.pm.mol^{-1}, determine what oxide (QO, Q_2O, Q_2O_3) that resulted from the reaction of Q and O. Distance of Q-O = 313 pm.

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Problem 4:

- Construct Born Haber cycle and determine the electron affinity of chlorine, if:
  - $\Delta H_{sublimation}$ (Mg) = 148 $kJ.mol^{-1}$
  - $\Delta H_{dissociation}$ (Cl) = 122 $kJ.mol^{-1}$
  - 1-st Ionization energy (Mg) = 738 $kJ.mol^{-1}$
  - 2-nd ionization energy (Mg) = 1451
  - Lattice energy ($MgCl_2$) = -2526 $kJ.mol^{-1}$
  - ΔH^o_f $MgCl_2$ = -641 $kJ.mol^{-1}$

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