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Electron Gain Enthalpy :- or Electron affinity

* When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the Electron Gain Enthalpy ($\Delta_{eg}H$).

* Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by following equation.

$$X(g) + 1e^- \longrightarrow X^-(g)$$

$$X + e^- \xrightarrow[\Delta_{eg}H_1]{} X^- \xrightarrow[\Delta_{eg}H_2]{+e^-} X^{2-} \xrightarrow[\Delta_{eg}H_3]{+1e^-} X^{3-}$$

$$\Delta_{eg}H_1 > \Delta_{eg}H_2 > \Delta_{eg}H_3$$

*** * Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic.

AIR * Group 17 elements (the halogen) has very high negative electron gain enthalpies because they can attain stable gas electronic configurations by picking up an electron.

AIR * Nobel gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

Variation of electron gain enthalpy :-

* The Variation in electron gain enthalpies of elements is less systematic than for ionisation enthalpies.

* As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge ↑ses from left to right across a period and therefore it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus.

* Electron gain enthalpy generally become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus.

Table 3.7 Electron Gain Enthalpies / (kJ mol⁻¹) of Some Main Group Elements

Group 1	$\Delta_{eg}H$	Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
H	− 73					He	+ 48
Li	− 60	O	− 141	F	− 328	Ne	+ 116
Na	− 53	S	− 200	Cl	− 349	Ar	+ 96
K	− 48	Se	− 195	Br	− 325	Kr	+ 96
Rb	− 47	Te	− 190	I	− 295	Xe	+ 77
Cs	− 46	Po	− 174	At	− 270	Rn	+ 68

AIR * However, electron gain enthalpy of 'O' or 'F' is less negative that of the succeding elements. This is because when an electron electron is added to 'O' or 'F', the added electron goes to smaller n=2 quantum level and suffers significant repulsion from the other electrons present in this level. For the n=3 quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

* $\Delta_{eg}H \rightarrow$ +ve for Nobel gases and alkaline earth metal.

Factors influencing EA Values :-

(i) Effective nuclear charge :- ↑es effective nuclear charge ↑es E.A.

(ii) size of atom :→ Greater is size of valence shell, lesser is EA.

(iii) Ellipticity of subshell :- EA of s > p > d > f

(iv) Nature of configuration :- EA_1 of C > EA_1 of N

* chlorine atom has highes EA
* EA of III period > EA of II period (for P-block elements)
* EA of 14 grp > 15 grp.
*

$N - N^{-1}$ = 7 kJ/mol $\quad$ $P - P^-$ = 72.02

$N^{-1} - N^{-2}$ = −673 kJ/mol. $\quad$ $P^- - P^{2-}$ = −418

$N^{-2} \rightarrow N^{-3}$ = −1070 kJ/mol $\quad$ $P^{2-} - P^{3-}$ = −886

* $O - O^-$ = 140.986 kJ/mol $\quad$ $S - S^-$ = 200.42

$O^- - O^{2-}$ = −744 kJ/mol $\quad$ $S^- \rightarrow S^{2-}$ = −456

{ EA +ve ⇒ if energy released }
{ EA −ve ⇒ if energy supplied }