# CH-105 INORGANIC TUTORIAL - I

## Topic-I

**Q-I.1.** The boiling point of the inert gases are as follows: He – 4 K , Ne – 10 K, Ar -100 K, Kr-170 K and Xe-220K. Rationalize the trend observed.

Ans:

He < Ne < Ar < Kr < Xe

As the size increases, the atom can be polarized easily, hence induced dipole-induced dipole interactions are stronger in Xe compared to He. Therefore, the boiling point increases down the group. The number of electrons that can contribute to the induced dipoles is also increasing as we go from He to Xe.

Point 1: Discuss about other weak interactions and their relative strength.

**Q-I.2.** Between the two reactions listed below, predict the following (i) in which direction the reaction equilibrium lies (ii) qualitatively predict which reaction is expected to be faster using the following absolute η values.

$$\underset{8.0}{HCl} + \underset{4.08}{LiH} \rightleftharpoons \underset{4.75}{LiCl} + \underset{8.7}{H_2}$$

$$\underset{7.82}{HOF} + \underset{4.08}{LiH} \rightleftharpoons \underset{5.87}{LiF} + \underset{9.5}{H_2O}$$

Ans: For first equation $\langle\eta\rangle_{LHS}$ is 6.04 $\langle\eta\rangle_{RHS}$ is 6.72 while for the second reaction $\langle\eta\rangle_{LHS}$ is 5.95 $\langle\eta\rangle_{RHS}$ is 7.68. Thus for both the reaction, the equilibrium lies on the right side. However, the difference between the $\langle\eta\rangle_{LHS}$ and $\langle\eta\rangle_{RHS}$ for the first reaction is 0.68, while for the second reaction is 1.73. Qualitatively, this suggests that the second reaction is expected to be faster. The experimental enthalpy of formation also supports these results (ΔH= -56.1 kcal/mol while for the second one, it is -144.1 kcal/mol).

**Q-I.3**. Predict the relative solubility trend in water for the following two sets of molecules. (a) NaF, NaCl, NaBr, NaI (b) CuF, CuCl, CuBr and CuI. Briefly rationalize your answer.

Ans:

The solubility of set a) will increase in the order of

NaF < NaCl < NaBr < NaI

For Set b) solubility will decrease in the order of

CuF > CuCl > CuBr > CuI.

Explanation:

This is due to the HSAB principle. i.e. Hard-acid and hard base adduct and soft base-soft acid adduct form stable complexes lead to least solubility in water.

**Q-I.4**. Using hard-soft concepts, which of the following reactions are predicted to have an equilibrium constant greater than 1? Unless otherwise stated, assume gas-phase or hydrocarbon solution and 25°C.

(a) $R_3PBBr_3 + R_3NBF_3 \rightleftharpoons R_3PBF_3 + R_3NBBr_3$

(b) $CH_3HgI + HCl \rightleftharpoons CH_3HgCl + HI$

(c) $[AgCl_2]^{2-}(aq) + 2\,CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) + 2\,Cl^-(aq)$

Ans:

**(a) $R_3P–BBr_3 + R_3N–BF_3 \rightarrow R_3P–BF_3 + R_3N–BBr_3$? <1**

R3P --- 5.7 ; BBr3 4.85 ; R3N ---6.3; BF3 --- 9.7

**a) $R_3P–BBr_3 + R_3N–BF_3 \rightleftharpoons R_3P–BF_3 + R_3N–BBr_3$:** You know that phosphines are softer bases than amines (see Table 5.4). To determine the position of this equilibrium, you must decide which Lewis acid is softer because the softer acid will preferentially form a complex with a soft base. Boron tribromide is a softer Lewis acid than $BF_3$, a consequence of the relative hardness and softness of the respective halogen substituents. Therefore, the equilibrium position for this reaction will lie to the left, the side with the soft–soft and hard–hard complexes and the equilibrium constant is less than 1. In general, it is found that soft substituents (or ligands) lead to a softer Lewis acid than for the same central element with harder substituents.

**b) $CH_3HgI + HCl \rightleftharpoons CH_3HgCl + HI$:** Iodide is a softer base than chloride, an example of the general trend that elements later in a group are softer. The soft acid $CH_3Hg^+$ will form a stronger complex with iodide than with chloride, whereas the hard acid $H^+$ will prefer chloride, the harder base. Thus, the equilibrium constant is less than 1.

**c) $[AgCl_2]^-(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) + 2Cl^-(aq)$:** Cyanide is a softer and generally stronger base than chloride. Therefore, cyanide will displace the relatively harder base from the soft Lewis acid $Ag^+$. The equilibrium constant is greater than 1.

(a) $R_3P–BBr_3 + R_3N–BF_3 \rightarrow R_3P–BF_3 + R_3N–BBr_3$? <1

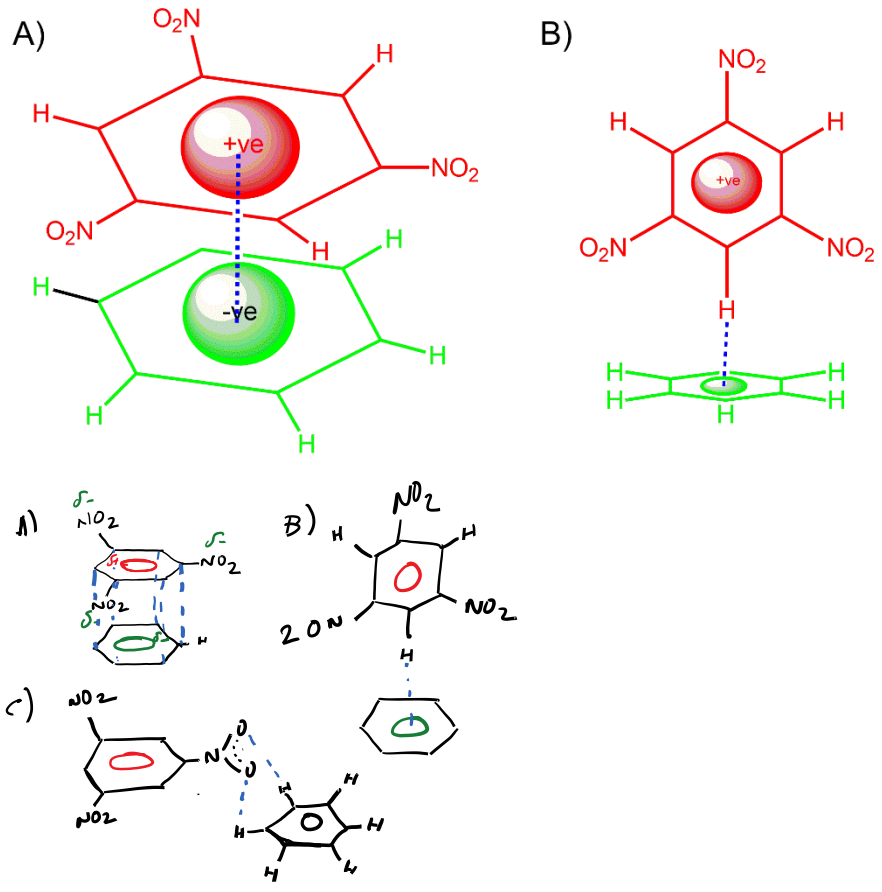
(b) $CH_3HgI + HCl \rightarrow CH_3HgCl + HI$? <1

(c) $[AgCl_2]^-(aq) + 2\,CN^-(aq) \rightarrow [Ag(CN)_2]^-(aq) + 2Cl^-(aq)$? >1

Note: R3P is soft base R3N is the hard base. As we go down in the group, the polarizability increases and hence the softness. A similar concept can also be used for other equations.

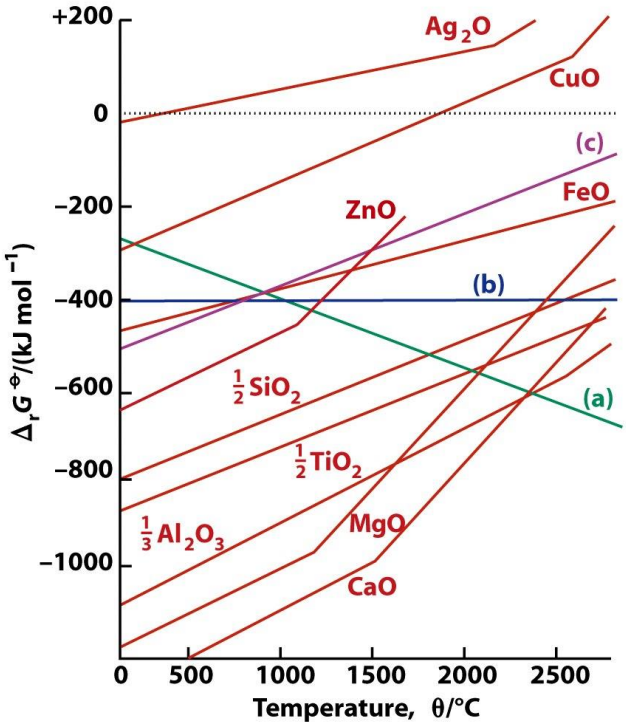
**Q-I.5**. Draw at least two possible interactions that can exist between 1,3,5-trinitrobenzene and benzene. Identify the most stable form.

Ans: There are at least three possible geometries as shown below. The most stable one is (A).

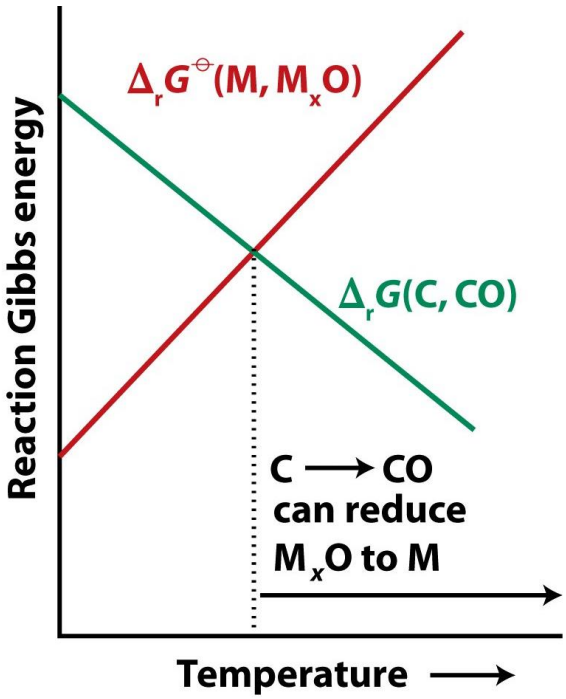


# Topic-II

**Q-II.1**. Why are the metals Al and Ti are not produced by pyrometallurgical extraction of $Al_2O_3$ and $TiO_2$? What will be a better method to produce such metals?




Carbon can reduce any metal oxide provided that the temperature is sufficiently high. The plot of C (C→CO) in Ellingham Diagram will intersect all the meta -metal oxide curves because of the reverse slope of the C line. However, the use of C (coke) becomes impracticable for the metal oxides towards the bottom of the Ellingham Diagram, e.g., CaO, $Al_2O_3$.




$Al_2O_3$ and $TiO_2$ have rather large negative heats of formation. Therefore, their heats of decomposition (i.e., Dissociation Energies) are correspondingly high. For $\Delta G^o$ to be negative, it requires that $T\Delta S^o$ term to be very large, which means the temperature must be very high. In effect, these substances are thermally very stable and resist decomposition.

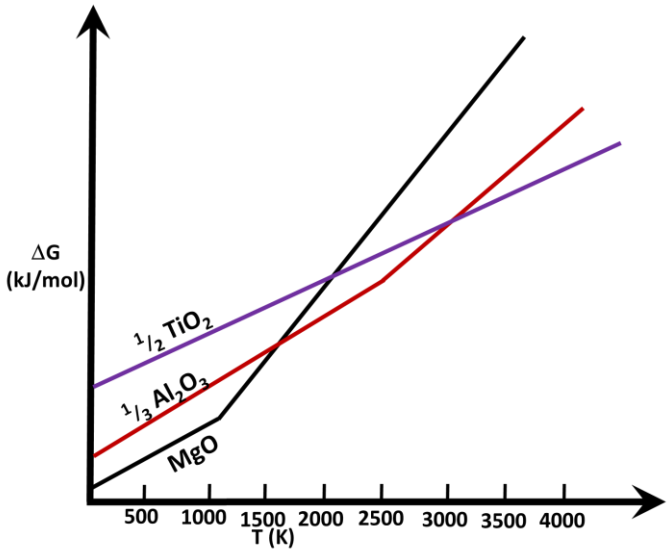
$Al_2O_3$ $\Delta H_f$ = -1676 KJ/mol; this energy is sufficient enough to melt the reaction products.

For example, $Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$ (liquid)

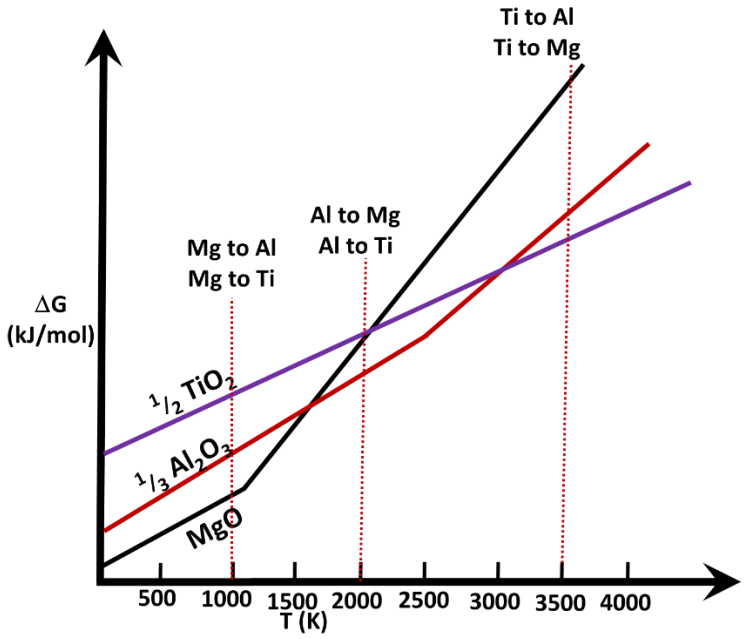
(a) This is called the thermite process, which is used for welding iron and steel.
(b) Thermit bombs used by the military as incendiary devices because of the intense heat of the reaction.

Al by electrolysis and Ti by Kroll/Van Arkel.

**Q-II.2**. The Ellingham diagram of metal oxides is given below. Depict how to obtain (a) Mg from MgO using Al and Ti metals (b) Al from $Al_2O_3$ using Mg and Ti metals (c) Ti from $TiO_2$ using Mg and Al in the graph given below.




Answer:




**Q-II.3**. To a silver nitrate solution, an aluminium rod is initially inserted. After ~20 minutes, a magnesium rod is inserted to the same solution. After another 20 minutes, $O_2$ is bubbled into the solution at a slightly elevated temperature. What are the products formed at each stage? (You may use the following redox potentials $Al^{3+}/Al$ = -1.66 V; $Ag^{+}/Ag$ = +0.80 V; $Mg^{2+}/Mg$ = -2.36 V; $O_2/2O^{2-}$ = + 1.36 V).

Ans: