Module 2 Defect Chemistry and Defect Equilibria

1. Write Schottky and Frenkel defect reactions in NaCl and AgBr respectively with appropriate charge notations.
2. Write the defect reactions in an oxide Mf_2O_3 at very high and very low oxygen pressures if oxygen and metal vacancies are dominant defects. Assume complete ionization of defects.
3. Many impurities have a tendency to dissolve in various oxides. If the impurity was an Mb_2O type oxide, what would be the possible defect reactions?
4. Show yourself how the defect concentration in a ceramic varies with temperature and activation energy. You can consider activation energies of 1, 1.5 and 2 eV at temperatures 300 K, 500K, 1000K and 1500 K.
5. For an oxide MO_2, do the following questions.
   (a) Write the defect reaction(s) in stoichiometric form assuming that Anti-Frenkel defects dominate.
   (b) Identify the dominating defects in the non-stoichiometric form at both high and low pO_2 and write the appropriate defect reaction(s).
   (c) Write the defect concentration dependence on the partial pressure of oxygen in all regions.
   (d) Draw a schematic log-log Brouwer's diagram with slopes of concentration vs pO_2 of each defect clearly written.
   (e) What would be expected type of conduction in this oxide and what would be dependence of conductivity on pO_2?
   (f) If the oxide has a band-gap of 5 eV and defect formation energy of 11 eV/f.u., what would be dominant mode of conduction at 1500K? Assume and state suitable numbers for mobilities of two modes (f.u.: formula unit).
   (g) What can be done with this oxide to make it a predominantly ionic conductor?
   (h) What voltage would be generated if this material is kept in an oxygen partial pressure gradient of 10^{-16}.

   Similar exercise can be performed for other types of oxides too.
6. Consider a material like MgO usually has Schottky defects with enthalpy of formation (ΔH_f) of about 7.7 eV. Its band gap is about 7.65 eV which decreases at a rate of 1 meV per K as MgO is heated. In case of an absolutely pure and stoichiometric MgO, which defects are likely to be created and present in higher concentrations at a temperature of 1673 K.
7. Predict the defect compensation for acceptor doping in TiO_2 and understand the effect of T, pO_2 and composition.
8. Write the defect reactions in $BaTiO_3$ change when oxygen pressure (pO_2) is changed i.e. very low pressures, intermediate pressures and very high pressures. Express the dependence of appropriate defect or carrier concentration in terms of pO_2. Assume that defects that can be present are oxygen and smaller cation vacancies and defects are fully ionized. Also it is noted that at intermediate pressures, due to presence of acceptor impurities in $BaTiO_3$, defect concentration is usually independent of oxygen pressure. Plot the carrier concentration vs pO_2.
9. Consider an oxide A_2O which is dominated by presence of metal and oxygen vacancies at appropriate pO_2. This oxide forms predominantly Schottky defects at the stoichiometric conditions (i.e. at moderate pO_2). Attempt the following and state any assumptions clearly.
   (a) Write possible defect reactions for this oxide at low, moderate (stoichiometric condition) and high pO_2.
   (b) Write down the rate constants for each regime with appropriate powers of concentration of relevant defects and pO_2. The rate constants for oxidation, reduction, intrinsic stoichiometric defect ionization, and intrinsic electronic ionization reactions can be depicted as K_O, K_R, K_S and K_i.

(c) Now derive expressions of the concentrations of the defects in each regime using the data from (a) and (b).

(d) Show that $pO_2 \gg [K_S^{8/3}/K_O^2]$ under high pO_2 conditions and $pO_2 \ll [K_R/4K_S]^2$ under low pO_2 conditions.

(e) Draw a qualitative Brouwer's Diagram (defect concentration vs pO_2, both on log scale) for this oxide. Depict the plot of each defect clearly with their slopes in each region.