

Define sparingly soluble salts

Salts having solubilities less than about 0.01 mole/lit in water at ordinary temp are called sparingly soluble salts. AgCl is an example of a sparingly soluble salt.

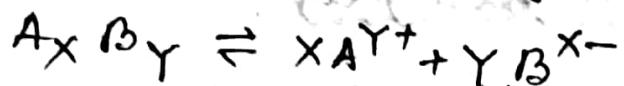
Define solubility product ( $K_{sp}$ ) and solubility product principle

It was experimentally found that in unsaturated solutions of sparingly soluble salt, the product of the concentrations of the constituent ions is a constant at a constant temp. This product is called solubility product of the salt.

Solubility Product Principle:

In a saturated solution of a sparingly soluble salt, the product of the concentration of the constituent ions is a constant at constant temp.

Thus for an electrolyte  $A_x B_y$ , ionising as  ~~$\rightarrow$~~

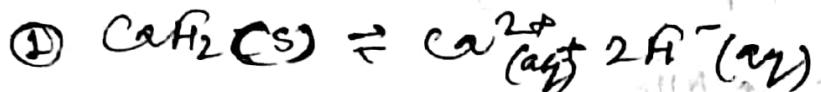


According to solubility Product principle,

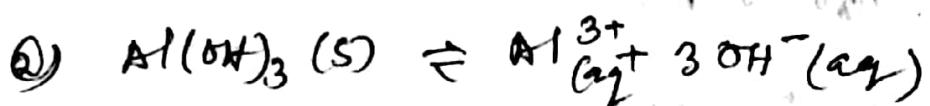
$$\boxed{x[A^{Y+}]^x} \boxed{[B^{X-}]^y} = \text{constant at constant temp}$$

$\Rightarrow K_{sp}$  of  $A_x B_y$  [  $K_{sp}$  = solubility prod]

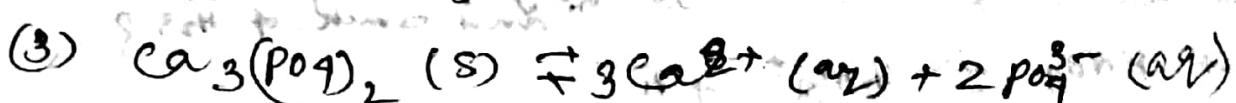
Q. Give an expression for  $K_{sp}$  of the following comp.



$$K_{sp} \text{ of } CaF_2 = [Ca^{2+}] [F^-]^2$$



$$K_{sp} \text{ of } Al(OH)_3 = [Al^{3+}] [OH^-]^3$$

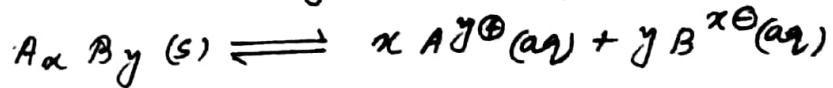


$$K_{sp} \text{ of } Ca_3(Po_4)_2 = [Ca^{2+}]^3 [Po_4^{3-}]^2$$

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Define solubility product of a sparingly soluble salt.

→ In a saturated solution of a sparingly soluble salt, a dynamic equilibrium exists between the insoluble salt and its dissociated ions. In general, for a salt of the type  $A_xB_y$  which in solution yields  $A^{x\oplus}$  and  $B^{x\ominus}$  ions according to the equilibrium:



on applying the law of mass action, the equilibrium constant is given by —

$$K_{eqm.} = \frac{a_x^{x\oplus} \cdot a_y^{x\ominus}}{a_{AxB_y}}$$

Since for the pure solid,  $a_{AxB_y} = 1$  and then  $K_{eqm.} = K_{sp}$ , where  $K_{sp}$  is called the solubility product constant or activity product. Therefore,

$$K_{sp} = c_{A^{x+}}^x \cdot c_{B^{x-}}^y$$

If a solution is saturated with a given salt, then product of the activities of its constituents ions raised to the appropriate power must be constant. This is called solubility product constant.

If the activity of each ion is written as the product of its concentration in gm-moles lit.<sup>-1</sup> and corresponding activity co-efficient, then we have

$$K_{sp} = (c_{A^{x+}}^x \cdot c_{B^{x-}}^y) (\gamma_{A^{x+}}^x \cdot \gamma_{B^{x-}}^y)$$

$$= (c_{A^{x+}}^x \cdot c_{B^{x-}}^y) \gamma_{\pm}^{(x+y)}$$

where  $\gamma_{\pm}$  is the mean ionic activity co-efficient of  $A^{x+}$  and  $B^{x-}$  ions in the solution.

Defining,  $K'_{sp} = c_{A^{x+}}^x \cdot c_{B^{x-}}^y$  and thus

$$K_{sp} = K'_{sp} \cdot \gamma_{\pm}^{(x+y)}$$

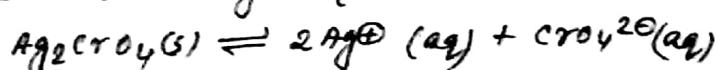
Unlike  $K_{sp}$  which is a constant at any given temperature,  $K'_{sp}$  is called concentration solubility product will vary with the activity co-efficient of  $A^{x+}$  and  $B^{x-}$  in the solution, i.e., with the ionic strength of the solution.

At low ionic strength, where the activity co-efficient approaches unity,  $K_{sp}$  and  $K'_{sp}$  are not greatly different. So that  $K'_{sp}$  defined above is approximately constant.

Any salt whether highly soluble or sparingly soluble will have a solubility product value. However,  $K_{sp}$  value of highly soluble salts are very high and they do not have any analytical applications.

Find out the relation between solubility and solubility product.

⇒ Let us consider the saturated solution of the salt  $Ag_2CrO_4$ , if solid salt is added, then in solution the following equilibrium exists:



on applying the law of mass action, the solubility