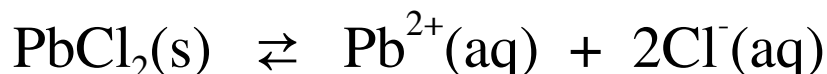


## Heterogeneous Equilibria & Le Châtelier's Principle

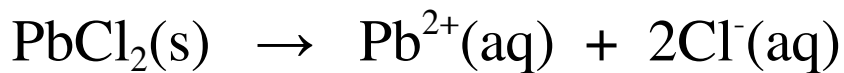
### Le Châtelier's Principle

when a stress is applied to a system, the system readjusts to relieve or offset the stress and the system reaches a new state of equilibrium

- consider the following equilibrium:

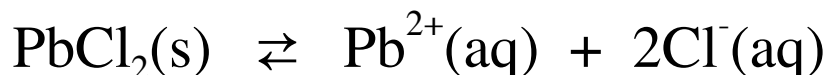


- the forward reaction is the **dissolving** reaction:



- > if we can cause the equilibrium to **SHIFT TO THE RIGHT** the rate of dissolving is increased more than the rate of crystallization
- > more solid  $\text{PbCl}_2$  will dissolve and the **solubility increases**

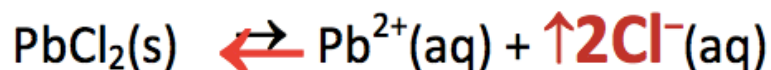
- consider the following equilibrium:



- > the solubility of the  $\text{PbCl}_2(\text{s})$  can be **decreased** by **increasing either  $[\text{Pb}^{2+}]$  or  $[\text{Cl}^{-}]$**
- > the  $[\text{Pb}^{2+}]$  can be increased by adding the soluble salt  $\text{Pb}(\text{NO}_3)_2$

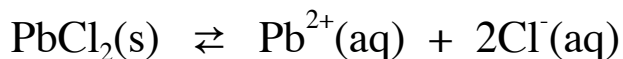


- > the  $[\text{Cl}^{-}]$  can be increased by adding the soluble salt  $\text{NaCl}$



COMMON ION EFFECT = decreasing the solubility of a salt by adding another salt with similar ions

- consider the following equilibrium:



add H<sub>2</sub>O

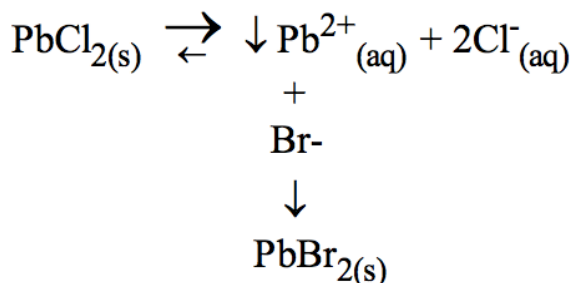
> the solubility of the  $\text{PbCl}_2(\text{s})$  can be **increased** by **decreasing either  $[\text{Pb}^{2+}]$  or  $[\text{Cl}^{-}]$**

> the  $[\text{Pb}^{2+}]$  can be decreased by adding some ion which precipitates the  $\text{Pb}^{2+}$

NaBr

- from Solubility Table -  $\text{Br}^{-}$ ,  $\text{I}^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{OH}^{-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$  will ppt  $\text{Pb}^{2+}$  (not  $\text{Cl}^{-}$  because already in equilibrium)

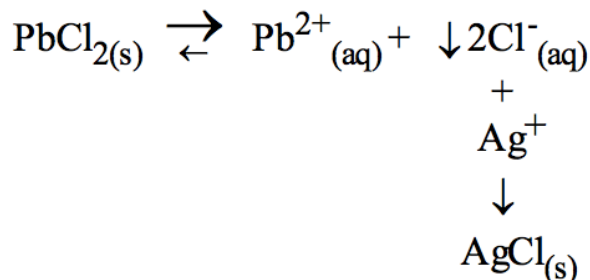
- add a soluble salt of  $\text{Br}^{-}$  such as NaBr:



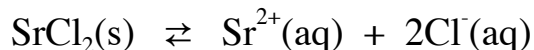
*NOTE: Precipitate must have a lower solubility than the  $\text{PbCl}_2$ .  $\text{PbCl}_2$  has  $K_{sp} = 1.2 \times 10^{-5}$  so  $K_{sp}$  of precipitate must be lower than this value.*

- similarly,  $\text{Ag}^{+}$  can be added as  $\text{AgNO}_3$  to decrease  $[\text{Cl}^{-}]$

$\text{CuNO}_3$

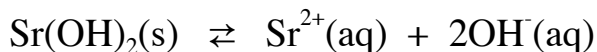


Q. What will happen to the equilibrium when the following chemicals are added?



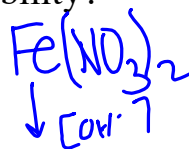
- a) 1 M ~~NaNO<sub>3</sub>~~ *no effect*
- b) 1 M ~~Na<sub>2</sub>SO<sub>4</sub>~~ *SrSO<sub>4</sub> ppt, ↓[Sr<sup>2+</sup>], shift R*
- c) 1 M ~~Sr(NO<sub>3</sub>)<sub>2</sub>~~ *↑[Sr<sup>2+</sup>], shift L, ↑solubility*
- d) 1 M ~~MgCl<sub>2</sub>~~ *↑[Cl<sup>-</sup>], shift L, sol ↓ ↓*

Q. Given the following equilibrium:



a) how could you **increase** the solubility?

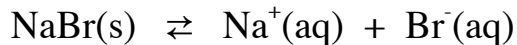
- add Na<sub>2</sub>SO<sub>4</sub> - ↓[Sr<sup>2+</sup>]*
- add H<sub>2</sub>O, add heat*
- \* ↓ [product]*



b) how could you **decrease** the solubility?

- ↑ [product] add NaOH*
- add Sr(NO<sub>3</sub>)<sub>2</sub>*

Q. What will happen to the equilibrium when the following chemicals are added?



- a) 1 M NaCl *↑[Na<sup>+</sup>] shift L ↓sol*
- b) 1 M AgNO<sub>3</sub> *AgBr ppt, ↓[Br<sup>-</sup>] shift R*
- c) 1 M KNO<sub>3</sub> *nothing - ↑sol*
- d) 1 M Na<sub>2</sub>SO<sub>4</sub>
- e) 2 M AgNO<sub>3</sub> *↑[Na<sup>+</sup>] shift L, ↓sol*

