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:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$

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

$$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)$$

> 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 $PbCl_2$ will dissolve and the **solubility increases**

- consider the following equilibrium:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$

> the solubility of the $PbCl_2(s)$ can be **decreased** by **increasing either [Pb^{2+}] or [Cl^-]**

> the [Pb^{2+}] can be increased by adding the soluble salt $Pb(NO_3)_2$

$$PbCl_2(s) \rightleftarrows \uparrow Pb^{2+}(aq) + 2Cl^-(aq)$$

> the [Cl^-] can be increased by adding the soluble salt NaCl

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + \uparrow 2Cl^-(aq)$$

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

- consider the following equilibrium:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$

add H_2O

> the solubility of the $PbCl_2(s)$ can be **increased** by **decreasing either $[Pb^{2+}]$ or $[Cl^-]$**

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

NaBr

– from Solubility Table - Br^-, I^-, SO_4^{2-}, S^{2-}, OH^-, PO_4^{3-}, CO_3^{2-}, SO_3^{2-} will ppt Pb^{2+} (not Cl^- because already in equilibrium)

- add a soluble salt of Br^- such as NaBr:

$$PbCl_{2(s)} \rightleftarrows \downarrow Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$$+ \; Br^- \;\downarrow\; PbBr_{2(s)}$$

NOTE: Precipitate must have a lower solubility than the $PbCl_2$. $PbCl_2$ has $K_{sp} = 1.2 \times 10^{-5}$ so K_{sp} of precipitate must be lower than this value.

CuNO3

- similarly, Ag^+ can be add as $AgNO_3$ to decrease $[Cl^-]$

$$PbCl_{2(s)} \rightleftarrows Pb^{2+}_{(aq)} + \downarrow 2Cl^-_{(aq)}$$

$$+ \; Ag^+ \;\downarrow\; AgCl_{(s)}$$

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

$$SrCl_2(s) \rightleftarrows Sr^{2+}(aq) + 2Cl^-(aq)$$

a) 1 M $NaNO_3$ no effect

b) 1 M Na_2SO_4 $SrSO_4$ ppt, ↓$[Sr^{2+}]$, shift R

c) 1 M $Sr(NO_3)_2$ ↑$[Sr^{2+}]$, shift L, ↑solubility ↓sol

d) 1 M $MgCl_2$

↑↑$[Cl^-]$, shifts L, Sol↓↓

Q. Given the following equilibrium:

$$Sr(OH)_2(s) \rightleftarrows Sr^{2+}(aq) + 2OH^-(aq)$$

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

add Na_2SO_4 – ↓$[Sr^{2+}]$

add H_2O, add heat

*↓[product]

$Fe(NO_3)_2$ ↓$[OH^-]$

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

↑[product] add NaOH

add $Sr(NO_3)_2$

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

$$NaBr(s) \rightleftarrows Na^+(aq) + Br^-(aq)$$

a) 1 M NaCl ↑$[Na^+]$ shift L ↓sol

b) 1 M $AgNO_3$ AgBr ppt, ↓$[Br^-]$ shift R - ↑sol

c) 1 M KNO_3 nothing

d) 1 M Na_2SO_4 ↑$[Na^+]$ shifts L, ↓sol

e) 2 M $AgNO_3$

more AgBr ppt ↓↓$[Br^-]$ ↑↑sol