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[TP] The expression for the equilibrium constant for the solubility equilibrium $M_2X(s) \rightleftharpoons 2 M^+(aq) + X^{2-}(aq)$ is ...

0% 1. $K_{sp} = [2 M^+][X^{2-}] / [M_2X]$
 0% 2. $K_{sp} = [2 M^+]^2 [X^{2-}] / [M_2X]$
 0% 3. $K_{sp} = [2 M^+]^2 [X^{2-}]$
 75% 4. $K_{sp} = [M^+]^2 [X^{2-}]$
 25% 5. Not sure

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Lecture 15 CH131 Summer 1 2021
 Wednesday, June 23, 2021

Chapter 16: Solubility equilibria

- Solubility equilibria
- Practice with solubility equilibria

Begin chapter 15: Acid-base equilibria

- The pH of water

Next lecture: Complete ch15; Begin ch17: Electrochemistry.

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Solubility equilibria

$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2 X^-(aq), K = K_{sp} = [M^{2+}][X^-]^2$

What is K_{sp} ? //

Solubility product.

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Solubility equilibria

$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2 X^-(aq), K = K_{sp}$

Five kinds of problems

- From K_{sp} → get solubility
- From solubility → get K_{sp}
- Solubility in presence of common ion
- Will precipitation occur? //
- What remains after precipitation?

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1. From $K_{sp} \rightarrow$ get solubility *✓ aqueous solution*
✓ 25°C

What is the **molar solubility** of CaF_2 ? $K_{sp} = 3.9 \times 10^{-11}$

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	excess	0	0
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$2x$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = (x)(2x)^2 = 4x^3$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \text{molar solubility}$$

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1. From $K_{sp} \rightarrow$ get solubility

What is the **molar solubility** of CaF_2 ? $K_{sp}/M^3 = 3.9 \times 10^{-11}$

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	excess	0	0
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$2x$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = (x)(2x)^2 = 4x^3$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \text{molar solubility}$$

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1. From $K_{sp} \rightarrow$ get solubility

What is the **molar solubility** of CaF_2 ? $K_{sp} = 3.9 \times 10^{-11}$

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	excess	0	0
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$2x$

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1. From $K_{sp} \rightarrow$ get solubility

What is the **molar solubility** of CaF_2 ? $K_{sp} = 3.9 \times 10^{-11}$

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	excess	0	0
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$2x$

$$K_{sp} = [\text{A}^{2+}][\text{X}^{-}]^2 = (x)(2x)^2 = 4x^3$$

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1. From K_{sp} → get solubility

What is the **molar solubility** of CaF_2 ? $K_{sp} = 3.9 \times 10^{-11}$

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial	excess	0	0
Change	-x	+x	+2x
Equilibrium	excess	x	2x

$$K_{sp} = [\text{A}^{2+}][\text{X}^-]^2 = (x)(2x)^2 = 4x^3$$

Answer: $0.00021 \text{ mol/L} = x = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}}$

Check: $0.00021 \times (2 \times 0.00021)^2 = 3.9 \times 10^{-11} = K_{sp}$

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2. From solubility → get K_{sp}

The solubility of magnesium phosphate is $0.000259 \text{ g}/100 \text{ g}$ of water at 20°C . Calculate its K_{sp} at this temperature.

$$\text{Mg}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Mg}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$$

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2. From solubility → get K_{sp}

The solubility of magnesium phosphate is $0.000259 \text{ g}/100 \text{ g}$ of water at 20°C . Calculate its K_{sp} at this temperature.

$$\text{Mg}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Mg}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$$

	$[\text{A}_3\text{X}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{3-}]$
Initial	excess	0	0
Change	-x	+3x	+2x
Equilibrium	excess	3x	2x

$$x = \frac{0.000259 \text{ g} \times \frac{1 \text{ mole}}{M_{\text{Mg}_3(\text{PO}_4)_2}}}{0.100 \text{ L}} = \text{a number}$$

$$K_{sp} = [\text{Mg}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3x)^3 (2x)^2 = 108x^5$$

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2. From solubility → get K_{sp}

The solubility of magnesium phosphate is $0.000259 \text{ g}/100 \text{ g}$ of water at 20°C . Calculate its K_{sp} at this temperature.

$$\text{Mg}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Mg}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$$

	$[\text{A}_3\text{X}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{3-}]$
Initial	excess	0	0
Change	-x	+3x	+2x
Equilibrium	excess	3x	2x

$0.000259 \text{ g}/100 \text{ g} \rightarrow \text{mol/L} = x$

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2. From solubility → get K_{sp}

The solubility of magnesium phosphate is 0.000259 g/100 g of water at 20 °C. Calculate its K_{sp} at this temperature.

$$\text{Mg}_3(\text{PO}_4)_2 (s) \rightleftharpoons 3 \text{Mg}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq)$$

	$[\text{A}_3\text{X}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{3-}]$
Initial	excess	0	0
Change	-x	+3x	+2x
Equilibrium	excess	3x	2x

$$K_{sp} = [\text{A}^{2+}]^3[\text{X}^{3-}]^2 = (3x)^3(2x)^2 = 108x^5$$

Answer: 1.00×10^{-23}

$[\text{PO}_4^{3-}] = 2.00 \times 10^{-23} \frac{\text{mol}}{\text{L}}$

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3. Solubility in presence of common ion

The molar solubility of CaF_2 , $K_{sp} = 3.9 \times 10^{-11}$, is 0.00021 mol/L. Calculate the molar solubility in a solution of 0.015 M NaF.

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

$[\text{F}^-] = 0.015$ 1L

$$\text{NaF}(s) \rightarrow \text{Na}^+(aq) + \text{F}^-(aq)$$

0.015 0.015

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3. Solubility in presence of common ion

The molar solubility of CaF_2 , $K_{sp} = 3.9 \times 10^{-11}$, is 0.00021 mol/L. Calculate the molar solubility in a solution of 0.015 M NaF.

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

net ionic equation ~

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial	excess	0	0.015
Change	-x	+x	+2x
Equilibrium	excess	x	0.015 + 2x

$$\text{NaF}(s) \rightarrow \text{Na}^+(aq) + \text{F}^-(aq)$$

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3. Solubility in presence of common ion

The molar solubility of CaF_2 , $K_{sp} = 3.9 \times 10^{-11}$, is 0.00021 mol/L. Calculate the molar solubility in a solution of 0.015 M NaF.

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial	excess	0	0.015
Change	-x	+x	+2x
Equilibrium	excess	x	0.015 + 2x

$$K_{sp} = 3.9 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(0.015 + 2x)^2 \approx x(0.015)^2$$

$$x = \frac{3.9 \times 10^{-11}}{(0.015)^2} = 0.0000017$$

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3. Solubility in presence of common ion

The molar solubility of CaF_2 , $K_{sp} = 3.9 \times 10^{-11}$, 0.00021 mol/L .
Calculate the molar solubility in a solution of 0.015 M NaF .

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	excess	0	0.015
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$0.015 + 2x$

$K_{sp} = [\text{A}^{2+}][\text{X}^{-}]^2 = (x)(0.015)^2 = x(0.015)^2$
Presence of common ion makes x smaller
Answer: 1.7×10^{-7} , 0.08 % of the value in pure water!
pure water: 0.00021 mol/L
 0.015 NaF : 0.0000017 mol/L

Common ion effect.

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4. Will precipitation occur?

0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in a total volume of 1.00 L of water. Will a precipitate form? $K_{sp} = 3.9 \times 10^{-11}$.

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	0	0.0100	0.00020

$0.00020 \text{ mol of NaF} \rightarrow 0.00020 \text{ mol F}^-$
 $0.0100 \text{ mol Ca(NO}_3)_2 \rightarrow 0.0100 \text{ mol Ca}^{2+}$
 $[\text{F}^-] = 0.00020 \text{ mol/L}$
 $[\text{Ca}^{2+}] = 0.0100 \text{ mol/L}$

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4. Will precipitation occur?

0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in a total volume of 1.00 L of water. Will a precipitate form? $K_{sp} = 3.9 \times 10^{-11}$.

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{-}]$
Initial	0	0.0100	0.00020

Is $[\text{A}^{2+}][\text{X}^{-}]^2 = (0.0100)(0.00020)^2 = Q_{sp} > K_{sp}$?
If no, then no precipitation.
If yes, then a precipitate will form.
Answer: $Q_{sp} = 4 \times 10^{-10} > K_{sp}$, so $\text{CaF}_2(s)$ will precipitate.

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5. What remains after precipitation

When 0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1.00 L of water, $\text{CaF}_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{sp} = 3.9 \times 10^{-11}$.

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5. What remains after precipitation

When 0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1.00 L of water, $\text{CaF}_2(\text{s})$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100	0.00020
Revised M	0.0001 mol	0.0099	0 //
Change	-y	+y	+2y
Equilibrium		0.0099 + y \approx 0.0099	2y //

$\text{Ca}^{2+} + 2\text{F}^- \rightarrow \text{CaF}_2(\text{s})$ 100% pptn.

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
I	0.0100	0.00020	
C	-0.0001	-0.00020	+0.00010
F	0.0099	0	0.00010

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5. What remains after precipitation

When 0.2 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1 L of water, $\text{CaF}_2(\text{s})$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100 mol	0.00020 mol //
Revised [...]			
Change			
Equilibrium			

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5. What remains after precipitation

When 0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1.00 L of water, $\text{CaF}_2(\text{s})$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100 mol	0.00020 mol
Revised [...]	0.0001 mol	0.0099 mol/V	0
Change			
Equilibrium			

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5. What remains after precipitation

When 0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1.00 L of water, $\text{CaF}_2(\text{s})$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100 mol	0.00020 mol
Revised [...]	0.0001 mol	0.0099 mol/V	0/V
Change	-y	+y	+2y
Equilibrium			

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5. What remains after precipitation

When 0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1.00 L of water, $\text{CaF}_2(\text{s})$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100 mol	0.0002 mol
Revised [...]	0.0001 mol	0.0099 mol/V	0/V
Change	-y	+y	+2y
Equilibrium	≈ 0.0001 mol	≈ 0.0099 mol/V	2y

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5. What remains after precipitation

When 0.20 mmol of NaF and 10.0 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1.00 L of water, $\text{CaF}_2(\text{s})$ precipitates. How much Ca^{2+} and F^- remain in solution?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

$0.0099 + y \approx 0.0099$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100 mol	0.0002 mol
Revised [...]	0.0001 mol	0.0099 mol/V	0/V
Change	-y	+y	+2y
Equilibrium	≈ 0.0001 mol	≈ 0.0099 mol/V	2y

$K_{\text{sp}} = [\text{A}^{2+}][\text{X}^-]^2 \approx (0.0099)(2y)^2$

Answer: $[\text{Ca}^{2+}] = 0.0099 \text{ M}$, $[\text{F}^-] = 2y = 0.000063 \text{ M}$

Check: $Q_{\text{sp}} = (0.0099)(0.000063)^2 = 3.9 \times 10^{-11} = K_{\text{sp}}$

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Practice with solubility equilibria

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[TP] The expression for the equilibrium constant for the solubility equilibrium $\text{M}_2\text{X}(\text{s}) \rightleftharpoons 2 \text{M}^+(\text{aq}) + \text{X}^{2-}(\text{aq})$ is ...

- 0% 1. $K_{\text{sp}} = [2 \text{M}^+][\text{X}^{2-}] / [\text{M}_2\text{X}]$
- 0% 2. $K_{\text{sp}} = [2 \text{M}^+]^2 [\text{X}^{2-}] / [\text{M}_2\text{X}]$
- 0% 3. $K_{\text{sp}} = [2 \text{M}^+]^2 [\text{X}^{2-}]$
- 100% 4. $K_{\text{sp}} = [\text{M}^+]^2 [\text{X}^{2-}]$ ✓
- 0% 5. Not sure

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[TP] K_{sp} for $M_2X(s) \rightleftharpoons 2M^+(aq) + X^{2-}(aq)$ is 8×10^{-11} . Assume a maximum of y moles of $M_2X(s)$ can dissolve in one liter. What is true in terms of y ?

0% 1. $K_{sp} = (2y)(y)$
 100% 2. $K_{sp} = (2y)^2(y)$ ✓
 0% 3. $K_{sp} = (y)^2(y)$
 0% 4. None of the above
 0% 5. Not sure

Handwritten notes:
 $M_2X(s) \rightleftharpoons 2M^+ + X^{2-}$
 I excess 0 0
 C -y +2y +y
 F none 2y y
 $K_{sp} = [M^+]^2 [X^{2-}] = (2y)^2 y$

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[TP] K_{sp} for $M_2X(s) \rightleftharpoons 2M^+(aq) + X^{2-}(aq)$ is 8×10^{-11} . Assume a maximum of y moles of $M_2X(s)$ can dissolve in one liter. What is true in terms of y if $M^+(aq)$ is initially $0.1 M$ (that is, M^+ is a common ion)?

0% 1. $K_{sp} = (2 \times 0.1 M)(y)$
 0% 2. $K_{sp} = (2 \times 0.1 M)^2(y)$
 100% 3. $K_{sp} = (0.1 M)^2(y)$ ✓
 0% 4. $K_{sp} = (0.1 M)(y)$
 0% 5. None of the above
 0% 6. Not sure

Handwritten notes:
 $M_2X(s) \rightleftharpoons 2M^+ + X^{2-}$
 I excess 0.1 0
 C -y +2y y
 F none 0.1+2y y
 $K_{sp} = [M^+]^2 [X^{2-}] = (0.1)^2 y$

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Chapter 15: Acid-base equilibria in aqueous solutions

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The pH of water

pH is defined as $-\log([H_3O^+])$.

The chemical equilibrium that accounts for the presence of H_3O^+ in water is

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ *autoionization of water*

$K \ll 1$ ✓
 $[H_3O^+] = [OH^-] \ll 1$ ✓

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The pH of water

Pure water at 50°C is measured to have a pH of 6.63.

This means that the value of the reaction quotient of the water autoionization at equilibrium at 50°C is

$$Q_e = K_w = [H_3O^+][OH^-] = (10^{-6.63})^2 = 5.48 \times 10^{-14}$$

$$pH = -\log([H_3O^+])$$

$$[H_3O^+] = 10^{-pH}$$

① pH = 6.63
 ② $[H_3O^+] = 10^{-6.63}$
 ③ Since $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
 ④ $K = K_w = [H_3O^+][OH^-]$
 ⑤ $K_w = 10^{-6.63} \times 10^{-6.63}$

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The pH of water

Pure water at 25°C is measured to have a pH of 7.00.

This means that the value of the reaction quotient of the water autoionization at equilibrium at 25°C is

$$Q_e = K_w = [H_3O^+][OH^-] = (10^{-7.00})^2 = 1.00 \times 10^{-14}$$

$$pH = -\log([H_3O^+])$$

$$[H_3O^+] = 10^{-pH}$$

① $[H_3O^+] = 10^{-7.00}$
 ② $[OH^-] = [H_3O^+] = 10^{-7.00}$
 pH = 7.00 = At 25°C, $K_w = 1.00 \times 10^{-14}$
 pH = 6.63 = At 50°C, $K_w = 5.48 \times 10^{-14}$

$$\Delta G = RT \ln(Q/K)$$

$$= \Delta H - T\Delta S$$

$$\Delta G^\circ = RT \ln(1/K)$$

$$= -RT \ln(K)$$

$$= \Delta H^\circ - T\Delta S^\circ$$

$$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

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[TP] The pH of pure water is different at different temperatures. This means that as temperature changes ...

At 25°C pH = 7.00
At 50°C pH = 6.63

- 0% the relative amounts of $H_3O^+(aq)$ and $OH^-(aq)$ in pure water change
- 0% the acidity of pure water changes
- 100% the value of the equilibrium constant changes
- 0% All the above
- 0% None of the above
- 0% Not sure

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

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