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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

132 ≤ 10
12 of 15 1 0

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1

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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2

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Solubility equilibria

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

What is K_{sp} ? *solubility product.*

$$K = [M^{2+}] [X^{-}]^2$$

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9

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Solubility equilibria

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

Five kinds of problems

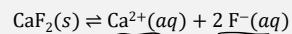
1. From K_{sp} → get solubility
2. From solubility → get K_{sp}
3. Solubility in presence of common ion
4. Will precipitation occur? //
5. What remains after precipitation?

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10

1. From K_{sp} → get solubility

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



*✓ aqueous solution
✓ 25°C*

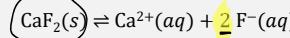
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11

11

1. From K_{sp} → get solubility

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



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

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

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

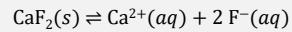
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12

12

1. From K_{sp} → get solubility

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



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

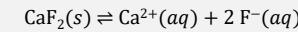
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13

13

1. From K_{sp} → get solubility

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



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

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14

14

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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	$2x$

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

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

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

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15

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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.

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

mol / 100 L

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16

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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	$3x$	$2x$

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

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

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17

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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	$3x$	$2x$

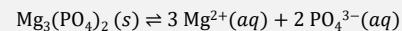
$$0.000259 \text{ g}/100 \text{ g} \rightarrow \text{mol/L} = x$$

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18

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.



	$[\text{A}_3\text{X}_2]$	$[\text{A}^{2+}]$	$[\text{X}^{3-}]$
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}

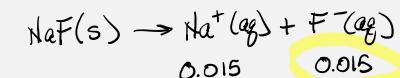
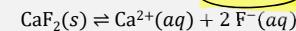
$$[\text{PO}_4^{3-}] = 2.00 \times 10^{-23} \text{ mol/l}$$

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19

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.

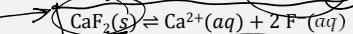


0.015 0.015

20

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.



net ionic
equation ~

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

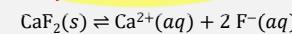


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21

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.



0.015 + 0.0000034

0.015 yes?

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

$$= (x)(0.015 + 2x)^2 \approx x(0.015)^2$$

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

22

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3. Solubility in presence of common ion

The molar solubility of CaF_2 , $K_{\text{sp}} = 3.9 \times 10^{-11}$, 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	$0.015 + 2x \approx 0.015$

Common ion effect.

$$K_{\text{sp}} = [\text{A}^{2+}][\text{X}^-]^2 = (x)(0.015)^2 = x(0.015)^2$$

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

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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? $K_{\text{sp}} = 3.9 \times 10^{-11}$.

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

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial	0	0.0106	0.00020

$0.00020 \text{ mol of NaF} \rightarrow 0.00020 \text{ mol F}^-$
 $0.0106 \text{ mol Ca}(\text{NO}_3)_2 \rightarrow 0.0106 \text{ mol Ca}^{2+}$
 $[\text{F}^-] = 0.00020 \text{ mol/L}$
 $[\text{Ca}^{2+}] = 0.0106 \text{ mol/L}$

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24

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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? $K_{\text{sp}} = 3.9 \times 10^{-11}$.

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

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

$[\text{A}^{2+}][\text{X}^-]^2 = (0.0100)(0.00020) = Q_{\text{sp}} > K_{\text{sp}}$?

If no, then no precipitation.
If yes, then a precipitate will form.

Answer: $Q_{\text{sp}} = 4 \times 10^{-10} > K_{\text{sp}}$, so $\text{CaF}_2(s)$ will precipitate //

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25

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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? $K_{\text{sp}} = 3.9 \times 10^{-11}$.

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26

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?

$$K_{\text{sp}} = 3.9 \times 10^{-11}$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
Initial mol	0	0.0100	0.00020
Revised M	0.00010 mol	0.0099	0.00020
Change	-y	+y	+2y
Equilibrium	0.00010 - 0.00020	0.0099 + y ≈ 0.0099	0.00020 + 2y

$\text{Ca}^{2+} + 2\text{F}^- \rightarrow \text{CaF}_2(s)$
 I: 0.0100 0.00020
 C: -0.0001 -0.00020
 F: 0.0099 0 0.00020

100% psta.

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27

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, $\text{CaF}_2(s)$ 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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28

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?

$$K_{\text{sp}} = 3.9 \times 10^{-11}$$

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

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29

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?

$$K_{\text{sp}} = 3.9 \times 10^{-11}$$

	$[\text{AX}_2]$	$[\text{A}^{2+}]$	$[\text{X}^-]$
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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30

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?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$.

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

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?
 $K_{\text{sp}} = 3.9 \times 10^{-11}$. $0.0099 + y \approx 0.0099$

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

$\frac{0.0099}{0.0001} = 99$ || $K_{\text{sp}} = [\text{A}^{2+}][\text{X}^-]^2 \approx (0.0099)(2y)^2$

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

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

Practice with solubility equilibria

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

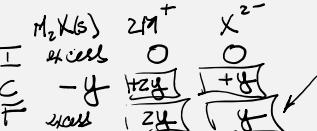
100% 2. $K_{sp} = (2y)^2(y)$

0% 3. $K_{sp} = (y)^2(y)$

0% 4. None of the above

0% 5. Not sure

$$K_{sp} = [M^+]^2 [X^{2-}] = (2y)^2 y$$



12 of 15 39 0

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39

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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. $K_{sp} = (2 \times 0.1 M)^2(y)$

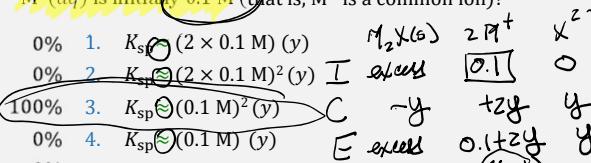
100% 3. $K_{sp} = (0.1 M)^2(y)$

0% 4. $K_{sp} = (0.1 M)(y)$

0% 5. None of the above

0% 6. Not sure

$$K_{sp} = [M^+]^2 [X^{2-}] = (0.1)^2 y$$



12 of 15 39 0

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40

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Chapter 15: Acid-base equilibria in aqueous solutions



41

41

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The pH of water

pH is defined as $\frac{1}{2} - \log([H_3O^+])$.

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

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

autoionization of water

$$K \ll 1$$

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



42

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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

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

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

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

$\text{① } \text{pH} = 6.63$

$\text{② } [H_3O^+] = 10^{-6.63}$

$\text{③ Since } H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$\text{④ } K = K_{w\text{,50}} = [H_3O^+] [OH^-]$

$\text{⑤ } K_w = 10^{-6.63} \times 10^{-6.63}$

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43

43

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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

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

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

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

$\text{① } [H_3O^+] = 10^{-7.00}$

$\text{② } [OH^-] = [H_3O^+] = 10^{-7.00}$

$\Delta G^\circ = RT \ln(\frac{P}{K})$

$= \Delta H - T\Delta S$

$\Delta G^\circ = RT \ln(\frac{P}{K})$

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

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

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

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44

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

At 25°C $\text{pH} = 7.00$
At 50°C $\text{pH} = 6.63$

0% 1. the relative amounts of $H_3O^+(aq)$ and $OH^-(aq)$ in pure water change

0% 2. the acidity of pure water changes

100% 3. the value of the equilibrium constant changes

0% 4. All the above

0% 5. None of the above

0% 6. Not sure

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

132510

12 of 15

48

0

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