

## Why is there equilibrium?

If the right handside of the reaction is lower in free energy why not all “products”?

If the left handside of the reaction is lower in free energy why not all “reactants”?

Entropy of mixing gives the mixture a slightly lower free energy than either extreme

some product + reactants will always be lower in G than all of one or the other

This is only true to compounds that “mix”

gases  
and  
solutions

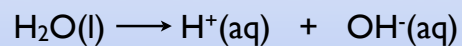
As a result  
solids and liquids do not appear in  
the equilibrium expression

For example



$$K = P_{\text{CO}_2}$$

No  $\text{CaCO}_3$  or  $\text{CaO}$   
they are solids  
for equilibrium you must have some  
solid but the amount doesn't matter



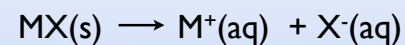
$$K = [\text{H}^+][\text{OH}^-]$$

(aq) is aqueous  
“dissolved in water”

No  $\text{H}_2\text{O}$  its a liquid

The simplest of all equilibria

Solubility



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

special name “solubility product”

$$K_{\text{sp}} = [\text{M}^+][\text{X}^-]$$

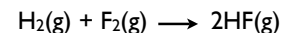
Easy to solve



R	M <sup>+</sup>	X <sup>-</sup>	
I	0	0	none in solution
C	+x	+2x	none in solution
E	+x	+2x	equilibrium is easy

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

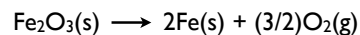
For the following reaction  $\Delta_{\text{R}}G^\circ = -542 \text{ kJ mol}^{-1}$  at 298K  
If I start out with a contain that has a pressure of  
1 atm of  $\text{H}_2(\text{g})$  and 1 atm of  $\text{F}_2(\text{g})$ ,  
at equilibrium what will the partial pressure of  $\text{HF}(\text{g})$  be?



- A. approximately 1 atm
- B. approximately 0 atm
- C. approximately 2 atm
- D. approximately 4 atm
- E. there is no way to know

K is really really big  
~ "to completion"

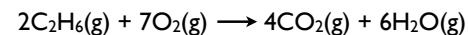
For the following reaction  $\Delta_{\text{R}}G^\circ = +740 \text{ kJ mol}^{-1}$  at 298K  
If I start out with a contain that has a pressure of  
1 mole of  $\text{Fe}_2\text{O}_3$ ,  
at equilibrium how much solid Fe will I have?



- A. approximately 0 moles
- B. approximately 1 moles
- C. approximately 2 moles
- D. approximately 3/2 moles
- E. there is no way to know

K is really really small  
~ "no products"

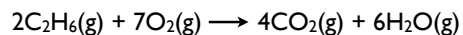
For the following reaction what is the change value for  $\text{H}_2\text{O}$ ?



R	$\text{C}_2\text{H}_6$	$\text{O}_2$	$\text{CO}_2$	$\text{H}_2\text{O}$
I	1.0	1.4	1.8	0
C	-2x	?	?	?

- A. -2x
- B. +2x
- C. +3x
- D. +6x

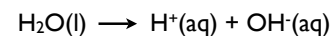
For the following reaction what is the equilibrium value for  $\text{CO}_2$ ?



R	$\text{C}_2\text{H}_6$	$\text{O}_2$	$\text{CO}_2$	$\text{H}_2\text{O}$
I	1.0	1.4	1.8	0
C	-5	?	?	?
E	?	?	?	?

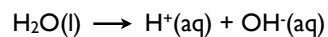
- A. 2.0  $-2x = -0.5$   
 $x=0.25$
- B. 1.4  $1.8+4x = 2.8$
- C. 2.8
- D.  $1.8 + 4x$

For this reaction which has a higher entropy?



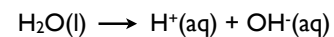
- A. the products
- B. the reactants
- C. they are the same

For this reaction which has a lower enthalpy?



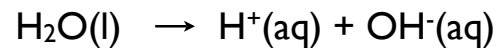
- A. the products
- B. the reactants
- C. they are the same

For this reaction which has a lower free energy?



- A. the products
- B. the reactants
- C. they are the same

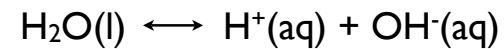
Liquid Water  
will spontaneously dissociate to a small extent



$$K = \frac{[\text{H}^+][\text{OH}^-]}{1}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

In water what is the concentration of  $[\text{H}^+]$ ?



$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

Pure Water

	$\text{H}^+$	$\text{OH}^-$
I	0	0
C	+x	+x
E	+x	+x

$$K_w = 10^{-14} = [\text{H}^+][\text{OH}^-] = (x)(x)$$

$$x = 10^{-7} \quad [\text{H}^+] = [\text{OH}^-] = 10^{-7}$$

pH

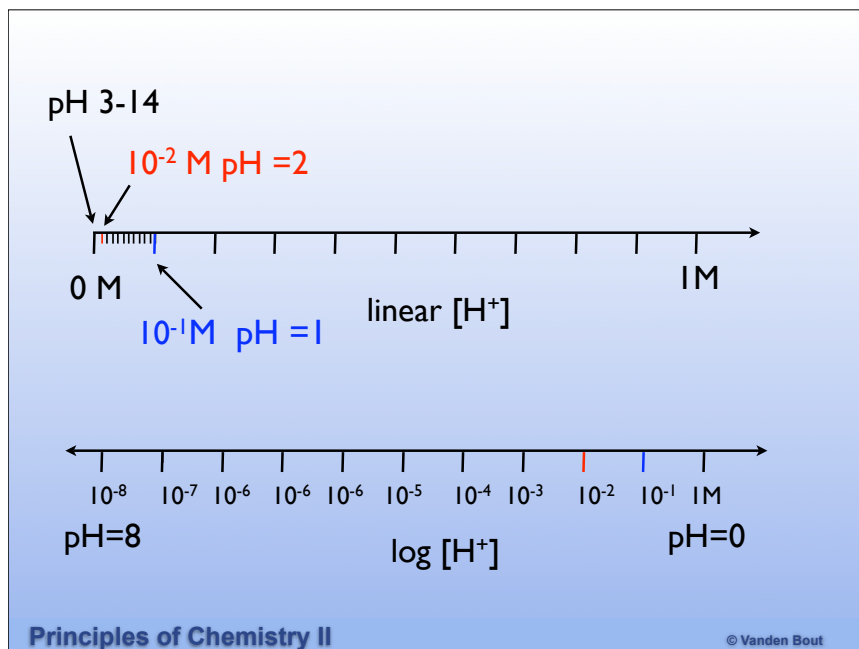
Log scale.  
Useful when dealing with very small  
or very large number (big ranges of numbers)  
every "pH" unit is 10x larger or smaller  $[\text{H}^+]$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = 13$$
$$[\text{H}^+] = 10^{-13}$$

$$\text{pH} = 7$$
$$[\text{H}^+] = 10^{-7}$$

$$\text{pH} = 2$$
$$[\text{H}^+] = 10^{-2}$$



## Acids and Bases

Brønsted-Lowry  
Definition

Acid is a proton ( $H^+$ ) donor

Base is a proton ( $H^+$ ) acceptor

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For example  
Hydrochloric Acid (HCl)

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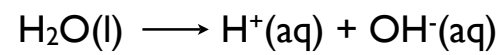
pH of pure water at 25°C

$x = 10^{-7}$   $[H^+] = [OH^-] = 10^{-7}$

$pH = -\log[H^+] = -\log(10^{-7}) = 7$

Neutral	Acidic	Basic
$[H^+] = [OH^-]$	$[H^+] > [OH^-]$	$[H^+] < [OH^-]$
at 25°C	at 25°C	at 25°C
pH = 7 pOH = 7	pH < 7 pOH > 7	pH > 7 pOH > 7

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This reaction is endothermic.  
Given that information what do you think  
the pH is for pure water at 60°C?

- A. 6.5 ←
- B. 7
- C. 7.5