Lecture 15 CH131 Summer 1

Tuesday, June 23, 2020

- Q algebra: Q (and so K) depends on how a reaction is written
- Disturbing equilibrium (Le Chatelier)

Begin ch 15: Acid-base equilibria

- The pH of water
- Weak acids and strong acids
- Pure strong acid
- Pure weak acid

Next lecture: Complete ch15; Ch16: Solubility equilibria

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The value of Q (and so K) depends on how a chemical reaction is written.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

$$K_1 = \frac{P_{CO_2} P_{H_2O}}{P_{CH_4} P_{O_2}^2}$$

$$\tfrac{1}{2}CH_4 + O_2 \rightarrow \tfrac{1}{2}CO_2 + H_2O$$

$$K_2 = \frac{P_{CO_2}^{1/2} P_{H_2O}}{P_{CH_4}^{1/2} P_{O_2}} = (K_1)^{1/2}$$

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Q depends on how a reaction is written

At a certain time, the value of the reaction quotient for the reaction

$2\ A + B \rightleftharpoons 2\ C$

is $Q_1 = 4.0$.

At the same time, what would be the value of Q be for the reaction

$4\ A + 2\ B \rightleftharpoons 4\ C$?

$Q_4 = (C)^4/((A)^4(B)^2) = (Q_1)^2 = 16$

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Q depends on how a reaction is written

At a certain time, the value of the reaction quotient for the reaction

$2\ A + B \rightleftharpoons 2\ C$

$$Q_1 = \frac{(C)^2}{(A)^2(B)}$$

is $Q_1 = 4.0$.

At the same time, what would be the value of Q be for the reaction

$2\ C \rightleftharpoons 2\ A + B$?

$$Q_2 = \frac{(A)^2(B)}{(C)^2}$$

$Q_2 = (A)^2(B)/(C)^2 = 1/Q_1 = 0.25$

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Q depends on how a reaction is written

At a certain time, here are the values of the reaction quotients for two different reactions,

$2\,A \rightleftharpoons B,\ \ Q_5 = (B)/(A)^2 = 2$

$C \rightleftharpoons 3\,D,\ \ Q_6 = (D)^3/(C) = 5$

At the same time, what would be the value of Q_7 for the reaction

$2\,A + C \rightleftharpoons B + 3D$?

$Q_7 = (B)(D)^3/((A)^2(C)) = \underline{Q_5} \times \underline{Q_6} = 10$

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[TP] The value of the equilibrium constant for the reaction

$2\,A \rightleftharpoons C$ is $K_1 = 4$

and that for the reaction

$D \rightleftharpoons C$ is $K_2 = 0.5$.

The value of the equilibrium constant for the reaction

$2\,A \rightleftharpoons D$ is $K_3 = \ldots$

19%	1.	2
0%	2.	4
13%	3.	6
69%	4.	8
0%	5.	None of the above

$\frac{1}{K_2} = \frac{1}{0.5} = 2$

$2A \rightleftharpoons C \quad K_1 = 4$

$C \rightleftharpoons D \quad 1/K_2 = 2$

$2A \rightleftharpoons D \quad (K_1)\left(\frac{1}{K_2}\right)$

$K_1 \times \frac{1}{K_2} = \frac{K_1}{K_2} \quad 4 \times 2 = 8$

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Disturbing equilibrium

Essential idea: A system at equilibrium responds to a disturbance by partially offsetting the disturbance.

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Disturbing equilibrium

Essential idea: A system at equilibrium responds to a disturbance by partially offsetting the disturbance.

This behavior is called Le Chatelier's principle.

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Practice: Problem 14.52

$Q = 0 < K = 2.4$

52. At $T = 100°C$ the reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

has an equilibrium constant $K = 2.4$.

(a) Suppose the initial partial pressure of SO_2Cl_2 is 1.20 atm, and $P_{SO_2} = P_{Cl_2} = 0$. Calculate the reaction quotient Q and state whether the reaction proceeds to the right or to the left as equilibrium is approached.

(b) Calculate the partial pressures at equilibrium.

(c) If the volume of the system is then decreased, will there be net formation or net dissociation of SO_2Cl_2?

	SO_2Cl_2	$\rightleftharpoons SO_2$	$+ Cl_2$	Q
I	1.20	0	0	0
C	$-x$	$+x$	$+x$	
E	$1.20 - x$	x	x	2.4

$2.4 = \dfrac{x^2}{1.20 - x} \Rightarrow x = 0.88$

E	0.38	0.88	0.88	$Q = 2.4$
I	2×0.38	2×0.88	2×0.88	
C	$+y$	$-y$	$-y$	
E	$2 \times 0.38 + y$	$2 \times 0.88 - y$	$2 \times 0.88 - y$	

Assume $V \rightarrow 1/2$, $P \rightarrow 2P$

$Q = \dfrac{P_{SO_2} P_{Cl_2}}{P_{SO_2Cl_2}} = \dfrac{2^2}{2} Q = 2Q$

$2Q > 2.4 = K$

$P_{total} = 2(0.38 + 0.88 + 0.88) - y$

$2(0.38 + 0.88 + 0.88)$

Chapter 15: Acid-base equilibria in aqueous solutions

The pH of water

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

The chemical equilibrium that accounts for the pH of water is

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

$Q = [H_3O^+][OH^-]$

The pH of water

Write down the reaction quotient for the water autoionization equilibrium.

$Q = [H_3O^+][OH^-]$

The pH of water

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

Write down the value of $[H_3O^+]$ at 50 °C.

$[H_3O^+] = 10^{-6.63} = 2.34 \times 10^{-7}$

$-\log([H_3O^+]) = 6.63$

$[H_3O^+] = 10^{-6.63}$

$[H_2O(l)] =$

$1\,L = 1000\,g$

$\frac{1\,mol}{18\,g} \times \frac{1000\,g}{L} = 55.6\,\frac{mol}{L}$

$\boxed{-\log([H_3O^+]) = pH \quad [H_3O^+] = 10^{-pH}}$

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The pH of water

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

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

Write down the value of $[OH^-]$ at 50°C.

$[OH^-] = [H_3O^+] = 10^{-6.63} = 2.34 \times 10^{-7}$

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The pH of water

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

Write down the value of the reaction quotient of the water autoionization at equilibrium at at 50°C.

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

$[OH^-] = 10^{-6.63}$

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What is an acid?

An acid makes $[H_3O^+] > [OH^-]$

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

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

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What is a base?

An base makes $[H_3O^+] < [OH^-]$

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

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

If $[H_3O^+] > [OH^-]$ acid
If $[H_3O^+] = [OH^-]$ neutral
If $[H_3O^+] < [OH^-]$ base

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[TP] Pure water at 50°C is measured to have a pH of 6.63. This means that at 50°C water is ...

41% 1. acidic
47% 2. neutral
12% 3. basic

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[TP] Pure water at 10°C has $[H_3O^+] = 5.39 \times 10^{-8}$.
This means that at 10°C water is ...

0% 1. acidic $[H_3O^+] > [OH^-]$
100% 2. neutral $[H_3O^+] = [OH^-]$
0% 3. basic $[H_3O^+] < [OH^-]$

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

$$[H_3O^+] = [OH^-] = 5.39 \times 10^{-8}$$

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[TP] Pure water at 25°C is measured to have a pH of 7.00. This means that at 25°C water is ...

0% 1. acidic
94% 2. neutral
6% 3. basic

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

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

0%	1. the relative amount of $H_3O^+(aq)$ and $OH^-(aq)$ in pure water change
0%	2. the acidity of pure water changes
71%	3. the value of the equilibrium constant changes
0%	4. All of the above
29%	5. None of the above

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

Assume ΔH and ΔS values at 25°C do not change w/ T.

$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\ln(K_2) - \ln(K_1)}{\frac{1}{T_2} - \frac{1}{T_1}}$

(1) $= \frac{\ln(K_2/K_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = \text{a number} = -\frac{\Delta H}{R} \Rightarrow \Delta H$

(2) Given ΔH, solve for ΔS using K_1, T_1 or K_2, T_2

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Weak acids and strong acids

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Strong acid equilibrium

Assume T = 25°C, $[H_3O^+] = 10^{-7}$

$c_a = 0.1$ M, $K_a = 1 \times 10^5$, $[H_3O^+] = 0.1$ M, % yield? $= \frac{\text{actual}}{\text{maximum}}\, 100\% = \frac{0.1\,M}{0.1\,M}\, 100\% = 100\%$

	$HA(aq)$ +	$H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$A^-(aq)$	
I	0.1	–	10^{-7}	0	Q
C	$-x$		$+x$	$+x$	0
E	$0.1-x$		$10^{-7}+x$	x	
	≈0		$=0.1\,M$		
			$x \approx 0.1\,M$		

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Weak acid equilibrium

25°C

$c_a = 0.1$ M, $K_a = 1 \times 10^{-5}$, $[H_3O^+] = 0.001$ M, % yield?

	HA +	H_2O ⇌	H_3O^+ +	A^-
I	0.1		10^{-7}	0
C	$-x$		$+x$	$+x$
E	$0.1-x$		$10^{-7}+x$	x
	$=0.1-0.001$		0.001	0.001

acid makes $[H_3O^+] > [OH^-]$

$\boxed{10^{-7} + x = 0.001 \quad x =}$

HCl = HA acid

Cl^- = A^- conjugate

$0.0000001 + x = 0.001$, $x = 0.001$

yield $= 100\% \frac{\text{actual}}{\text{max}} = 100\% \frac{0.001}{0.1} = 1\%$

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ / $A^- + H_2O \rightleftharpoons HA + OH^-$ ↑

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Solving acid and base equilibria

- Pure strong acid → assume 100% yield
- Pure weak acid → must solve equilibrium
- Partially neutralized weak acid $HA + OH^- \rightarrow H_2O + A^-$ LR
- Exactly neutralized weak acid
- Neutralized weak acid with excess base

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Pure strong acid

$c_a = 0.1$, 25°C, $K_a = 1\times10^5$ 1.00×10^{-7}

$c_a = 10.$

$[H_3O^+] = 10.$

$\boxed{pH = -1}$

$10^{-7} + 0.1 = 0.1$

$0.1 - y \approx 0.1$

$0.1 - 0.0000001 \approx 0.1$ ✓

	HA	$+ H_2O \rightleftharpoons$	H_3O^+	$+ A^-$	Q
I	0.1		10^{-7}	0	0
RI	0		0.1	0.1	∞
C	$+y$		$-y$	$-y$	
E	y		$0.1-y \approx 0.1$	$0.1-y \approx 0.1$	K_a

$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(0.1)^2}{y}$

$y = \frac{10^{-2}}{1\times10^5} = 1\times10^{-7}$

$[H_3O^+] = 0.1$ M $[HA] = 1\times10^{-7}$ M

$pH = -\log(0.1) = 1$

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Pure weak acid

$c_a = 0.1$ M, 25°C, $K_a = 1\times10^{-5}$

	HA	$+ H_2O \rightleftharpoons$	H_3O^+	$+ A^-$
I	0.1		10^{-7}	0
C	$-x$		$+x$	$+x$
E	$0.1-x$		$10^{-7}+x$	x

$K_a \ll 1$

$\boxed{K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(10^{-7}+x)(x)}{0.1-x}}$ ⇒ get two roots. But we know $x \gg 10^{-7}$, $10^{-7}+x \approx x$

$K_a \approx \frac{x^2}{0.1}$ ‖ $x = [H_3O^+] \approx \sqrt{0.1\,K_a} = 0.001$ ‖ $pH = 3$ ‖

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ $K_a = 1\times10^{-5}$

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_w = 1\times10^{-14}$

Since $K_a \gg K_w$ ⇒ $x \gg 10^{-7}$

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Weak acid K_a values

We can get the numerical value of K_a by analyzing the acid equilibrium.

	$HA(aq)$	$H_3O^+(aq)$	$A^-(aq)$	Q
Initial	c_a	10^{-7}	0	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$c_a - x$	$10^{-7}+x$	x	K_a
Approximate	$\approx c_a$	$\approx x$	x	K_a

With these simplifications, the acid equilibrium constant is …

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{c_a} = \frac{(10^{-pH})^2}{c_a}$$

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Weak acid K_a values

We can get the numerical value of K_a by analyzing the acid equilibrium.

	$HA(aq)$	$H_3O^+(aq)$	$A^-(aq)$	Q
Initial	c_a	10^{-7}	0	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$c_a - x$	$10^{-7} + x$	x	K_a
Approximate	$\approx c_a$	$\approx x$	x	K_a

For example, if $c_a = 0.10$ and $\mathrm{pH} = 4$, then …

$$K_a = \frac{(10^{-\mathrm{pH}})^2}{c_a} = \frac{(10^{-4.0})^2}{0.10} = 1.0 \times 10^{-7}$$

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