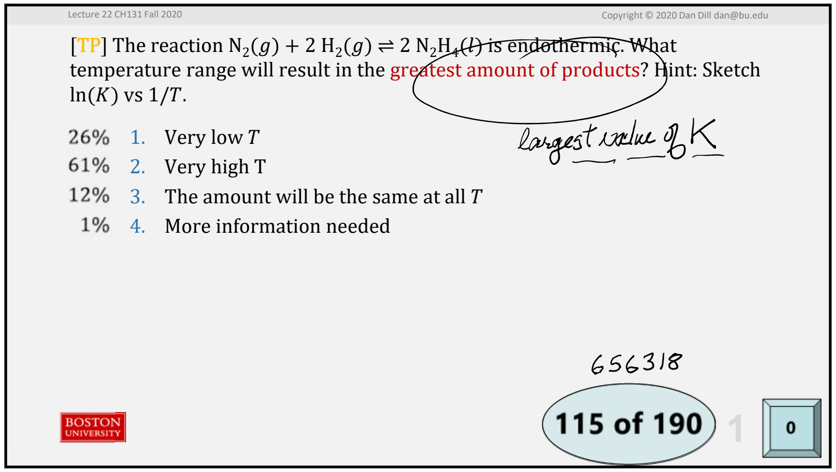


Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

[TP] The reaction $N_2(g) + 2\ H_2(g) \rightleftharpoons 2\ N_2H_4(l)$ is endothermic. What temperature range will result in the greatest amount of products? Hint: Sketch $\ln(K)$ vs $1/T$.

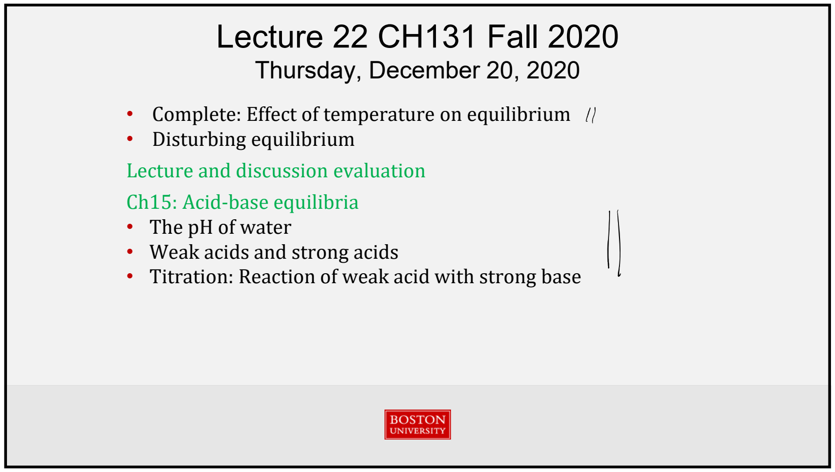
largest value of K

26%	1.	Very low T
61%	2.	Very high T
12%	3.	The amount will be the same at all T
1%	4.	More information needed

656318

115 of 190 1 0

1



Lecture 22 CH131 Fall 2020

Thursday, December 20, 2020

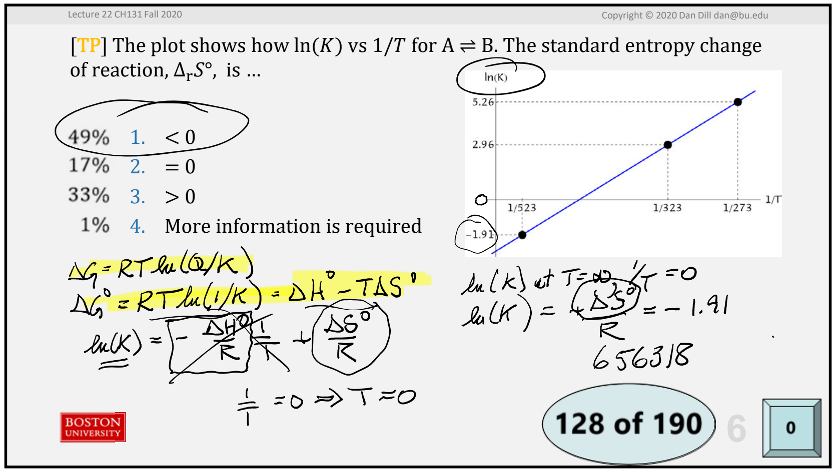
- Complete: Effect of temperature on equilibrium //
- Disturbing equilibrium

Lecture and discussion evaluation

Ch15: Acid-base equilibria

- The pH of water
- Weak acids and strong acids
- Titration: Reaction of weak acid with strong base

2



Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

[TP] The plot shows how $\ln(K)$ vs $1/T$ for $A \rightleftharpoons B$. The standard entropy change of reaction, $\Delta_r S°$, is …

49%	1.	< 0
17%	2.	$= 0$
33%	3.	> 0
1%	4.	More information is required

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

$\Delta G° = RT\ln(1/K) = \Delta H° - T\Delta S°$

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

$\frac{1}{T} = 0 \Rightarrow T = 0$

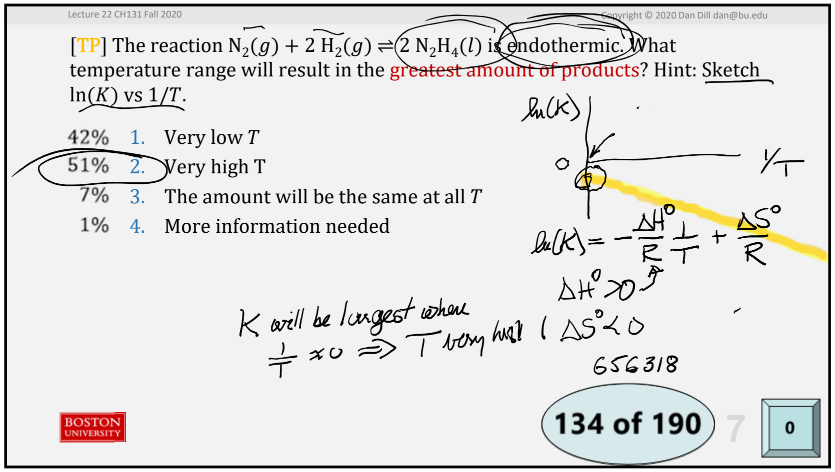
$\ln(K)$ at $T = \infty$ $1/T = 0$

$\ln(K) = +\frac{\Delta S°}{R} = -1.91$

656318

128 of 190 6 0

6



Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

[TP] The reaction $N_2(g) + 2\ H_2(g) \rightleftharpoons 2\ N_2H_4(l)$ is endothermic. What temperature range will result in the greatest amount of products? Hint: Sketch $\ln(K)$ vs $1/T$.

42%	1.	Very low T
51%	2.	Very high T
7%	3.	The amount will be the same at all T
1%	4.	More information needed

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

$\Delta H° > 0$

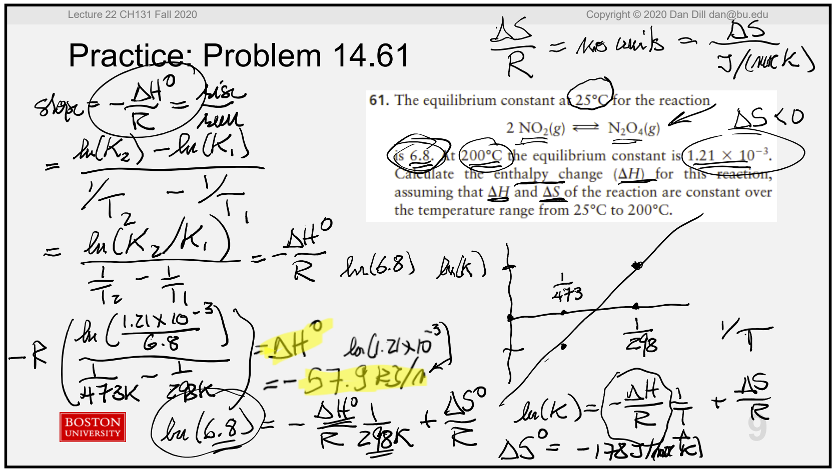
K will be largest when

$\frac{1}{T} \approx 0 \Rightarrow T$ very high ($\Delta S° < 0$

656318

134 of 190 7 0

7



Practice: Problem 14.61

61. The equilibrium constant at 25°C for the reaction

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

is 6.8. At 200°C the equilibrium constant is 1.21×10^{-3}. Calculate the enthalpy change (ΔH) for this reaction, assuming that ΔH and ΔS of the reaction are constant over the temperature range from 25°C to 200°C.

$$\frac{\Delta S}{R} = \text{no units} \Rightarrow \frac{\Delta S}{J/(mol\,K)}$$

$\Delta S < 0$

$$\text{slope} = \boxed{-\frac{\Delta H^\circ}{R}} = \frac{\text{rise}}{\text{run}} = \frac{\ln(K_2) - \ln(K_1)}{1/T_2 - 1/T_1} = \frac{\ln(K_2/K_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = -\frac{\Delta H^\circ}{R}$$

$$-R\left(\frac{\ln\left(\frac{1.21\times10^{-3}}{6.8}\right)}{\frac{1}{473K} - \frac{1}{298K}}\right) = \Delta H^\circ = -57.9\ kJ/mol$$

$\ln(6.8)$ $\ln(1.21\times10^{-3})$

$$\ln(6.8) = -\frac{\Delta H^\circ}{R}\frac{1}{298K} + \frac{\Delta S^\circ}{R}$$

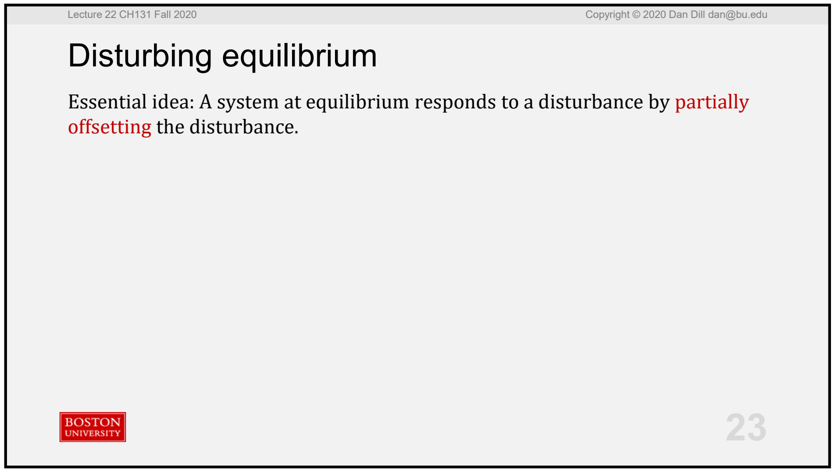
$$\ln(K) = \left(-\frac{\Delta H}{R}\right)\frac{1}{T} + \frac{\Delta S}{R}$$

$$\Delta S^\circ = -178\ J/(mol\,K)$$

BOSTON UNIVERSITY

9

9



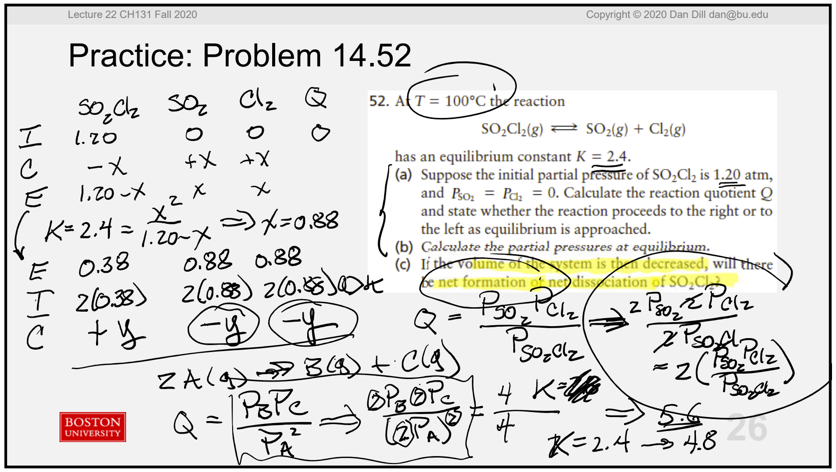
Disturbing equilibrium

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

BOSTON UNIVERSITY

23

23



Practice: Problem 14.52

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	SO_2	Cl_2	Q
I	1.20	0	0	0
C	−x	+x	+x	
E	1.20−x	x	x	

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

E	0.38	0.88	0.88
T	2(0.38)	2(0.88)	2(0.88)
C	+y	−y	−y

$$2A(g) \rightleftharpoons B(g) + C(g)$$

$$Q = \boxed{\frac{P_B P_C}{P_A^2} \Rightarrow \frac{2P_B\,2P_C}{(2P_A)^2}} = \frac{4}{4}K$$

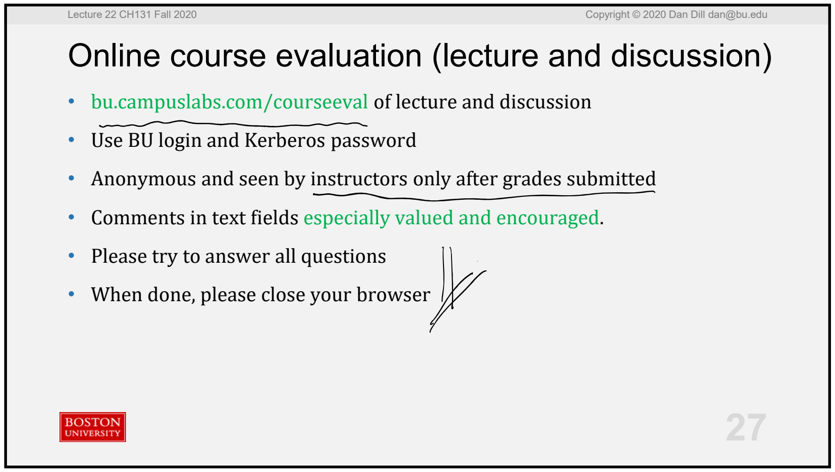
$$Q = \frac{P_{SO_2} P_{Cl_2}}{P_{SO_2Cl_2}} \Rightarrow \frac{2P_{SO_2}\,2P_{Cl_2}}{2P_{SO_2Cl_2}} = 2\left(\frac{P_{SO_2}P_{Cl_2}}{P_{SO_2Cl_2}}\right) \Rightarrow 5.6$$

$K = 2.4 \rightarrow 4.8$

BOSTON UNIVERSITY

26

26



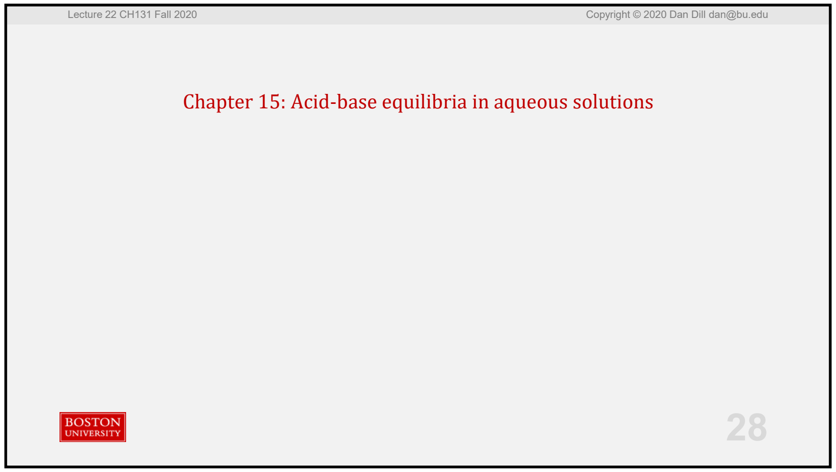
Online course evaluation (lecture and discussion)

- bu.campuslabs.com/courseeval of lecture and discussion
- Use BU login and Kerberos password
- Anonymous and seen by instructors only after grades submitted
- Comments in text fields especially valued and encouraged.
- Please try to answer all questions
- When done, please close your browser

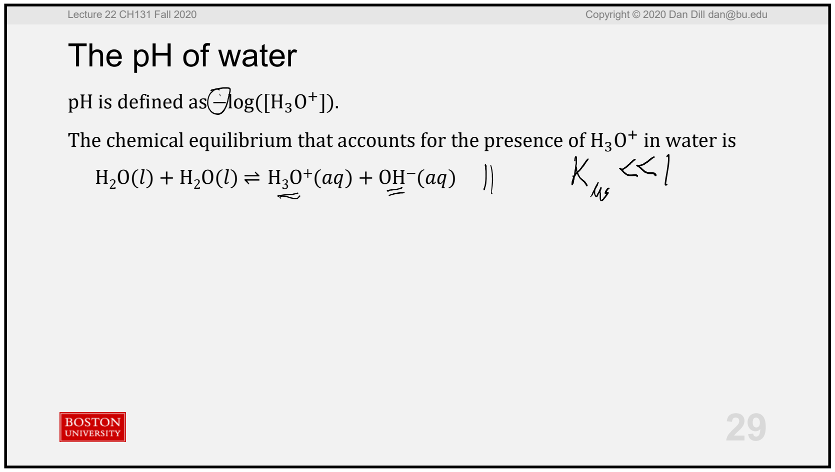
BOSTON UNIVERSITY

27

27



Chapter 15: Acid-base equilibria in aqueous solutions

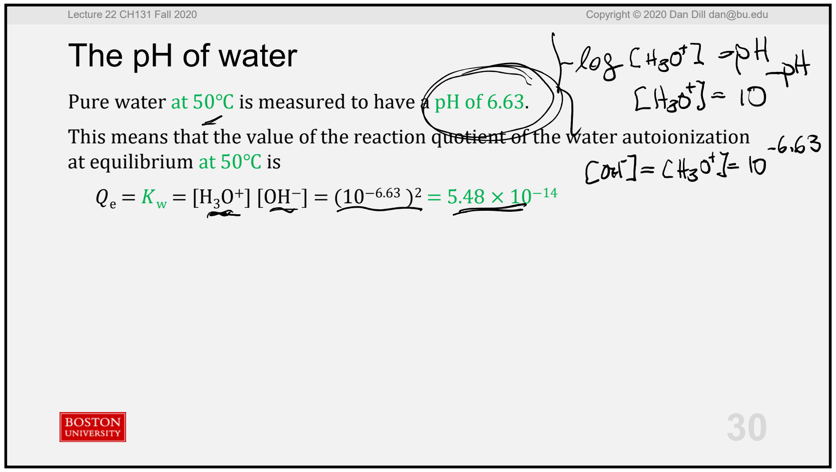


The pH of water

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

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

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad \| \qquad K_w \ll 1$$



The pH of water

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

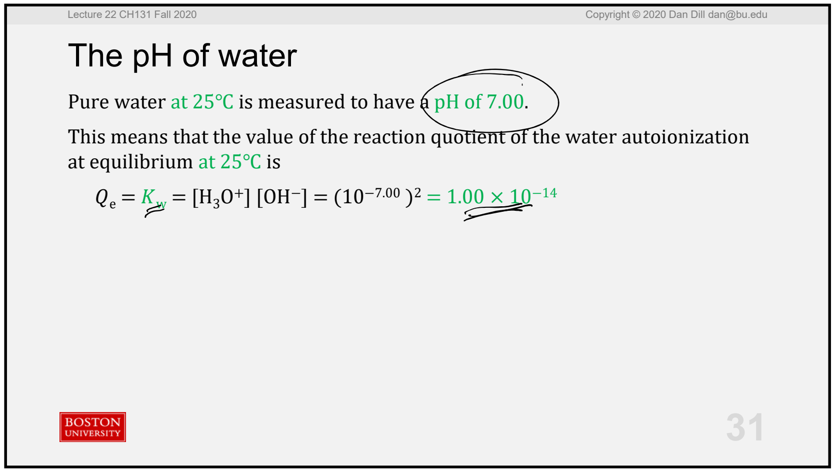
$-\log[H_3O^+] = pH$

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

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

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

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

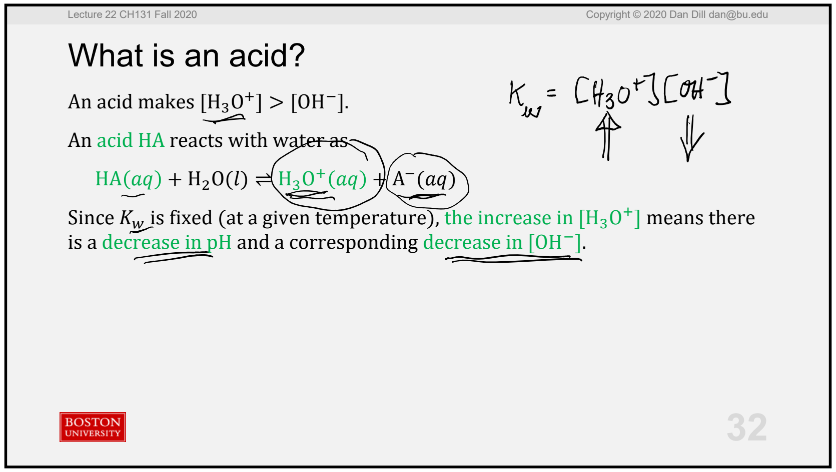


The pH of water

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

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



What is an acid?

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

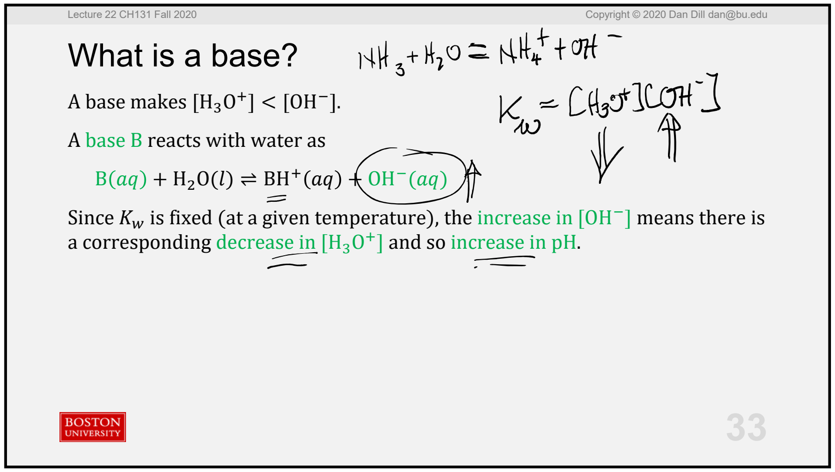
⇑ ⇓

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

An acid HA reacts with water as

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

Since K_w is fixed (at a given temperature), the increase in $[H_3O^+]$ means there is a decrease in pH and a corresponding decrease in $[OH^-]$.



What is a base?

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

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

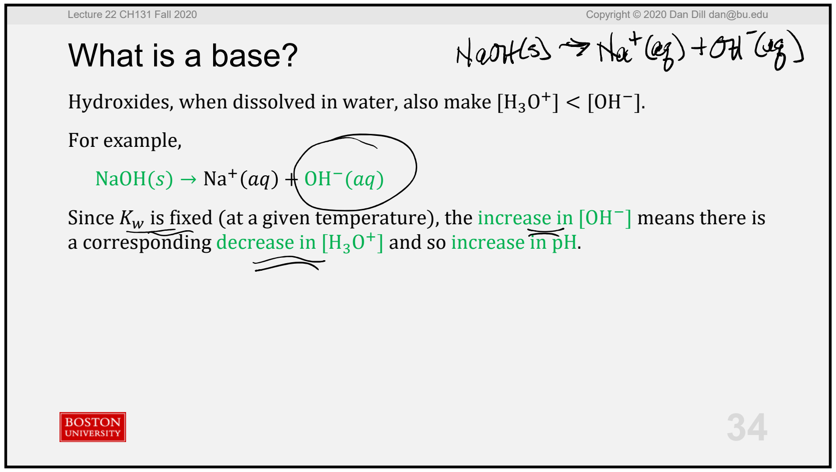
⇓ ⇑

A base makes $[H_3O^+] < [OH^-]$.

A base B reacts with water as

$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$ ⇑

Since K_w is fixed (at a given temperature), the increase in $[OH^-]$ means there is a corresponding decrease in $[H_3O^+]$ and so increase in pH.



What is a base?

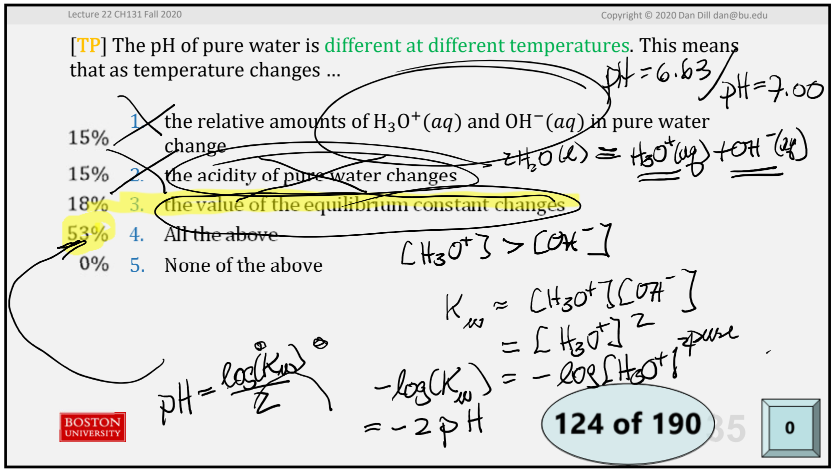
$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

Hydroxides, when dissolved in water, also make $[H_3O^+] < [OH^-]$.

For example,

$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

Since K_w is fixed (at a given temperature), the increase in $[OH^-]$ means there is a corresponding decrease in $[H_3O^+]$ and so increase in pH.



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

pH = 6.63 / pH = 7.00

15% 1. the relative amounts of $H_3O^+(aq)$ and $OH^-(aq)$ in pure water change

15% 2. the acidity of pure water changes

18% 3. the value of the equilibrium constant changes

53% 4. All the above

0% 5. None of the above

$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

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

$K_w \approx [H_3O^+][OH^-]$

$= [H_3O^+]^2$

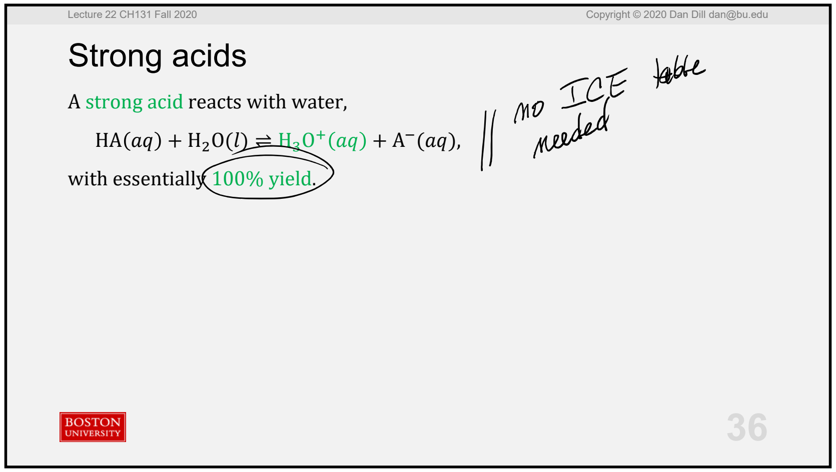
$-\log(K_w) = -\log[H_3O^+]^2_{pure}$

$= -2pH$

$pH = \frac{\log(K_w)}{2}$

124 of 190

0



Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

Strong acids

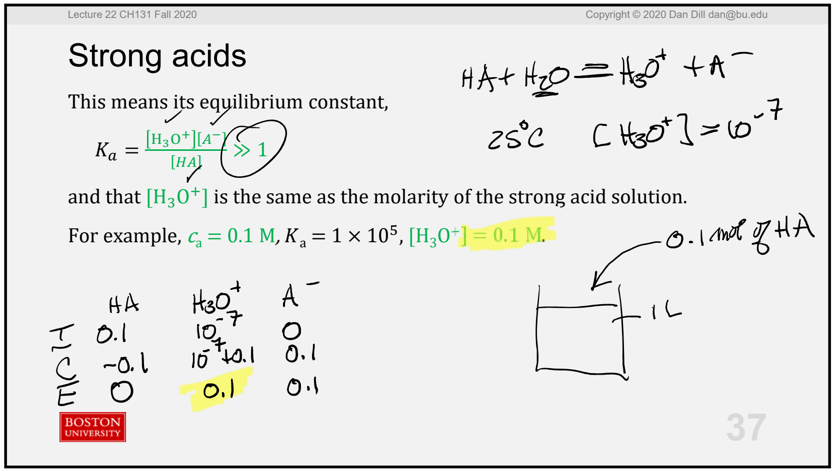
A strong acid reacts with water,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq),$$

with essentially 100% yield.

|| no ICE table needed

36



Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

Strong acids

This means its equilibrium constant,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \gg 1$$

and that $[H_3O^+]$ is the same as the molarity of the strong acid solution.

For example, $c_a = 0.1$ M, $K_a = 1 \times 10^5$, $[H_3O^+] = 0.1$ M.

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

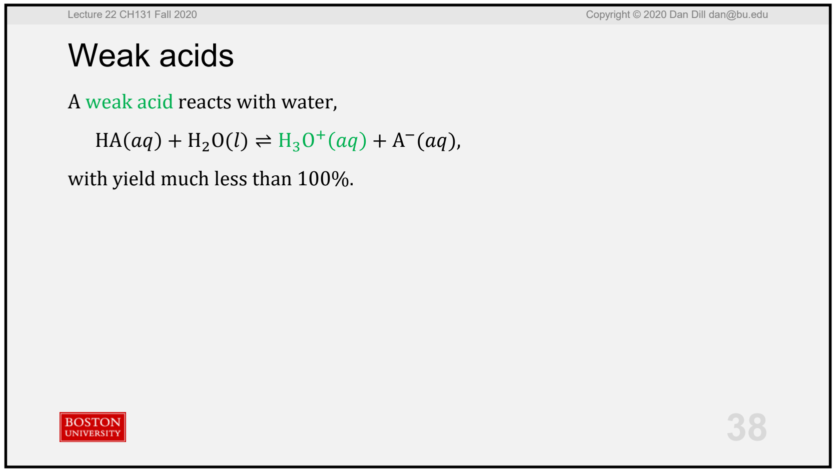
25°C $[H_3O^+] = 10^{-7}$

0.1 mol of HA

1L

	HA	H_3O^+	A^-
I	0.1	10^{-7}	0
C	−0.1	10^{-7} +0.1	0.1
E	0	0.1	0.1

37



Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

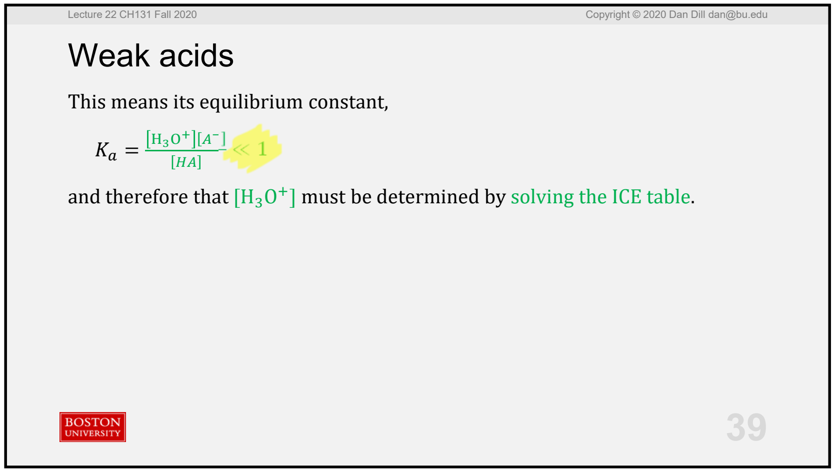
Weak acids

A weak acid reacts with water,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq),$$

with yield much less than 100%.

38



Lecture 22 CH131 Fall 2020 Copyright © 2020 Dan Dill dan@bu.edu

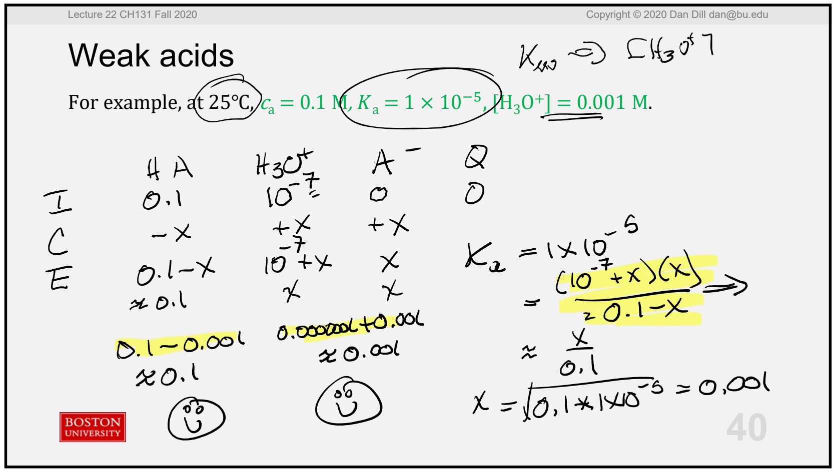
Weak acids

This means its equilibrium constant,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \ll 1$$

and therefore that $[H_3O^+]$ must be determined by solving the ICE table.

39



Weak acids

$K_w \Rightarrow [H_3O^+]$

For example, at 25°C, $c_a = 0.1$ M, $K_a = 1 \times 10^{-5}$, $[H_3O^+] = 0.001$ M.

	HA	H_3O^+	A^-	Q
I	0.1	10^{-7}	0	0
C	−x	+x	+x	
E	0.1−x ≈0.1	10^{-7}+x x	x x	

0.1−0.001 ≈0.1

0.0000001+0.001 ≈0.001

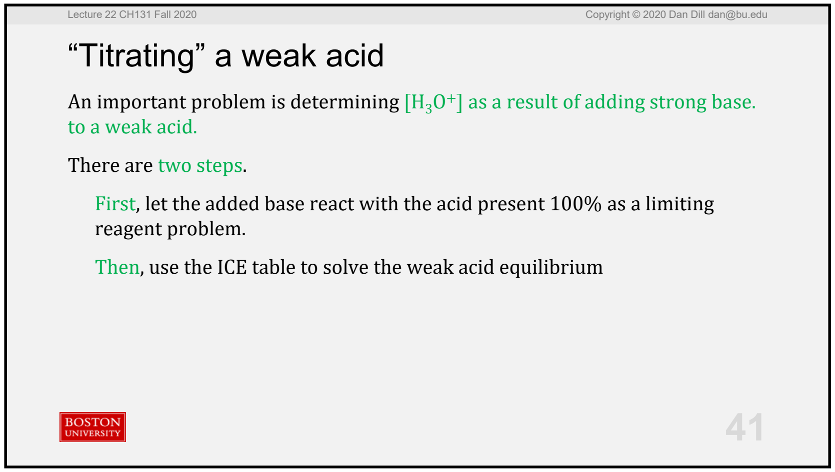
$$K_a = 1\times10^{-5} = \frac{(10^{-7}+x)(x)}{\approx 0.1-x} \Rightarrow \approx \frac{x}{0.1}$$

$$x = \sqrt{0.1 * 1\times10^{-5}} = 0.001$$

BOSTON UNIVERSITY

40

40



"Titrating" a weak acid

An important problem is determining $[H_3O^+]$ as a result of adding strong base. to a weak acid.

There are two steps.

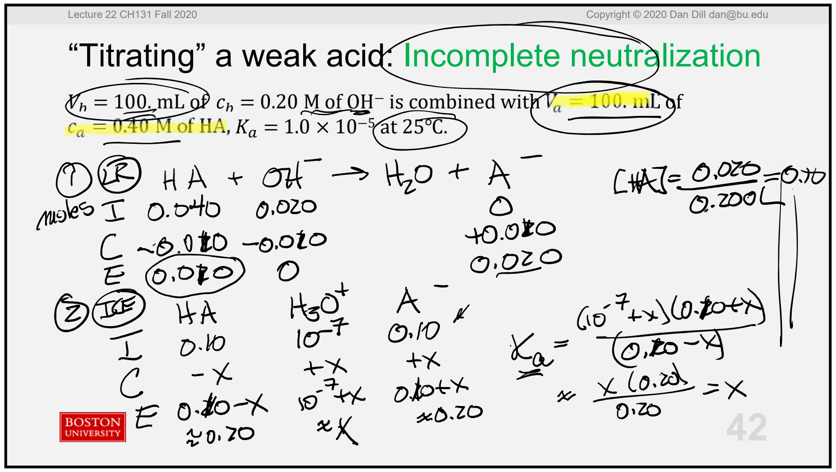
First, let the added base react with the acid present 100% as a limiting reagent problem.

Then, use the ICE table to solve the weak acid equilibrium

BOSTON UNIVERSITY

41

41



"Titrating" a weak acid: Incomplete neutralization

V_b = 100. mL of c_b = 0.20 M of OH^- is combined with V_a = 100. mL of c_a = 0.40 M of HA, $K_a = 1.0 \times 10^{-5}$ at 25°C.

① LR $HA + OH^- \rightarrow H_2O + A^-$

moles	HA	OH^-	A^-
I	0.040	0.020	0
C	−0.020	−0.020	+0.020
E	0.020	0	0.020

$$[HA] = \frac{0.020}{0.200\,L} = 0.10$$

② ICE

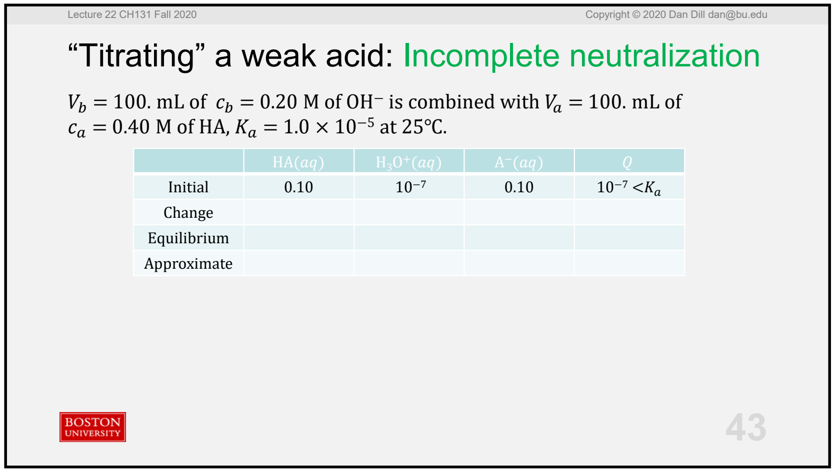
	HA	H_3O^+	A^-
I	0.10	10^{-7}	0.10
C	−x	+x	+x
E	0.20−x ≈0.20	10^{-7}+x ≈x	0.10+x ≈0.20

$$K_a = \frac{(10^{-7}+x)(0.20+x)}{(0.20-x)} \approx \frac{x\,(0.20)}{0.20} = x$$

BOSTON UNIVERSITY

42

42



"Titrating" a weak acid: Incomplete neutralization

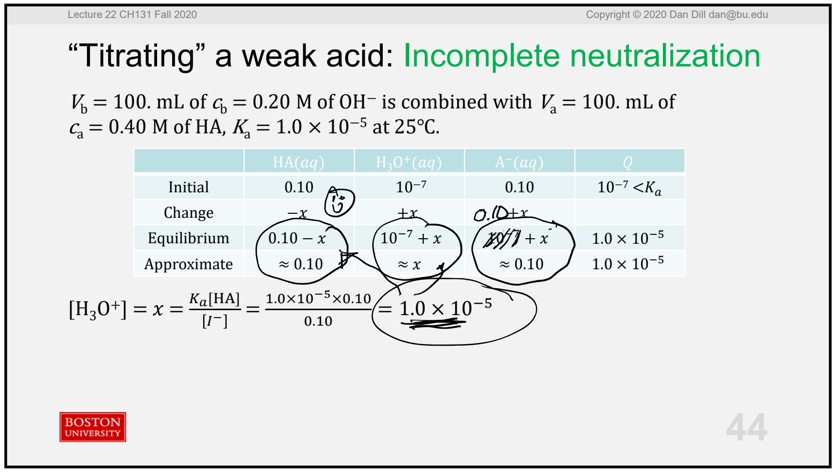
V_b = 100. mL of c_b = 0.20 M of OH^- is combined with V_a = 100. mL of c_a = 0.40 M of HA, $K_a = 1.0 \times 10^{-5}$ at 25°C.

	HA(*aq*)	$H_3O^+(aq)$	$A^-(aq)$	*Q*
Initial	0.10	10^{-7}	0.10	$10^{-7} < K_a$
Change				
Equilibrium				
Approximate				

BOSTON UNIVERSITY

43

43



Lecture 22 CH131 Fall 2020

"Titrating" a weak acid: Incomplete neutralization

$V_b = 100.$ mL of $c_b = 0.20$ M of OH^- is combined with $V_a = 100.$ mL of $c_a = 0.40$ M of HA, $K_a = 1.0 \times 10^{-5}$ at 25°C.

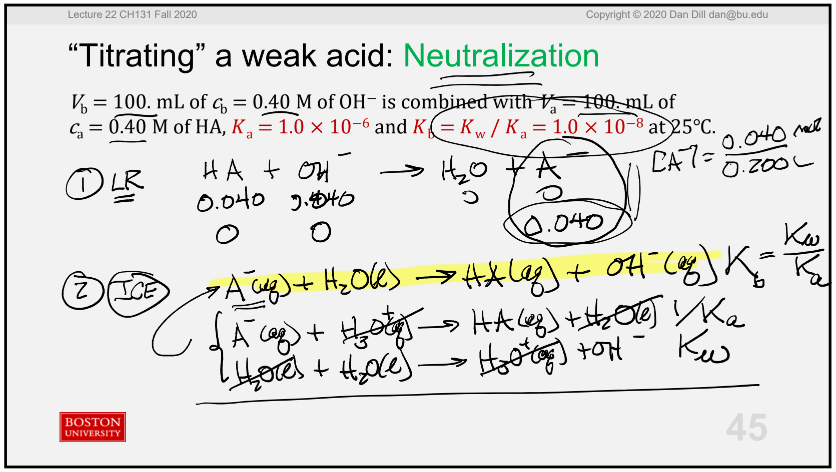
	$HA(aq)$	$H_3O^+(aq)$	$A^-(aq)$	Q
Initial	0.10	10^{-7}	0.10	$10^{-7} < K_a$
Change	$-x$	$+x$	$0.10 + x$	
Equilibrium	$0.10 - x$	$10^{-7} + x$	~~10^{-7}~~ $+ x$	1.0×10^{-5}
Approximate	≈ 0.10	$\approx x$	≈ 0.10	1.0×10^{-5}

$$[H_3O^+] = x = \frac{K_a[HA]}{[I^-]} = \frac{1.0\times10^{-5}\times0.10}{0.10} = \underline{1.0 \times 10^{-5}}$$

BOSTON UNIVERSITY

44

44



Lecture 22 CH131 Fall 2020

"Titrating" a weak acid: Neutralization

$V_b = 100.$ mL of $c_b = 0.40$ M of OH^- is combined with ~~$V_a = 100.$ mL of~~ $c_a = 0.40$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = K_w / K_a = 1.0 \times 10^{-8}$ at 25°C.

① LR

$$HA + OH^- \rightarrow H_2O + A^-$$

0.040 0.040 0 0

0 0 0.040

$$[A^-] = \frac{0.040 \text{ mol}}{0.200 \text{ L}}$$

② ICE

$$A^-(aq) + H_2O(l) \rightarrow HA(aq) + OH^-(aq) \quad K_b = \frac{K_w}{K_a}$$

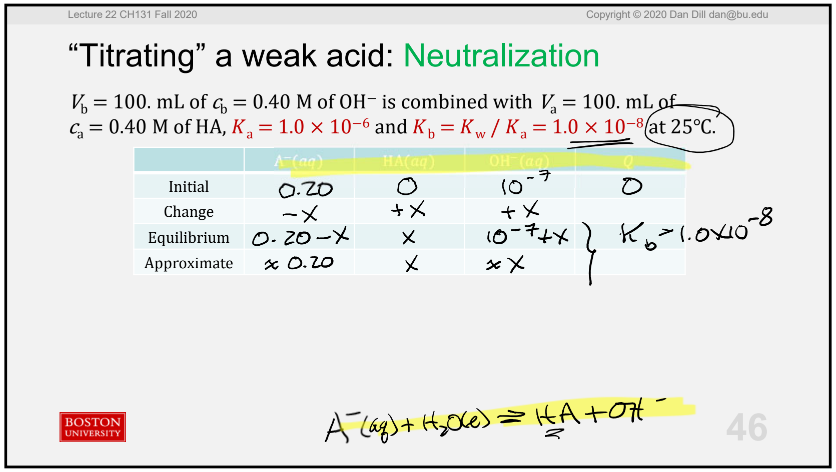
$$A^-(aq) + \cancel{H_3O^+(aq)} \rightarrow HA(aq) + \cancel{H_2O(l)} \quad 1/K_a$$

$$\cancel{H_2O(l)} + H_2O(l) \rightarrow \cancel{H_3O^+(aq)} + OH^- \quad K_w$$

BOSTON UNIVERSITY

45

45



Lecture 22 CH131 Fall 2020

"Titrating" a weak acid: Neutralization

$V_b = 100.$ mL of $c_b = 0.40$ M of OH^- is combined with $V_a = 100.$ mL of $c_a = 0.40$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = K_w / K_a = 1.0 \times 10^{-8}$ at 25°C.

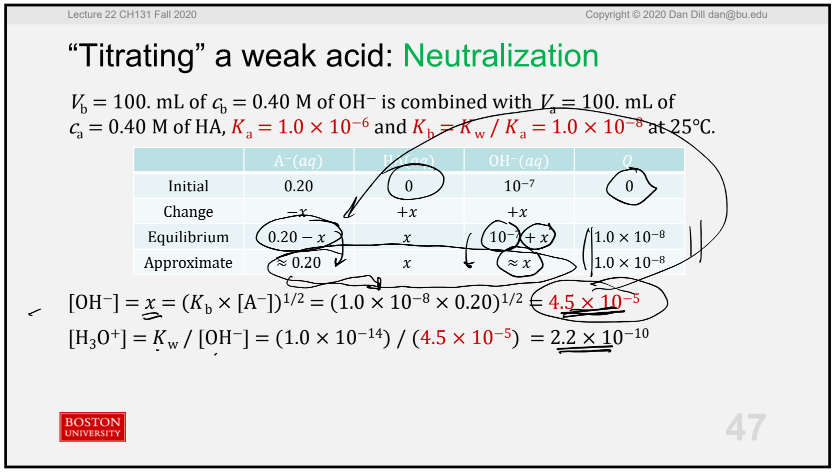
	$A^-(aq)$	$HA(aq)$	$OH^-(aq)$	Q
Initial	0.20	0	10^{-7}	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$0.20 - x$	x	$10^{-7} + x$	$K_b = 1.0 \times 10^{-8}$
Approximate	≈ 0.20	x	$\approx x$	

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

BOSTON UNIVERSITY

46

46



Lecture 22 CH131 Fall 2020

"Titrating" a weak acid: Neutralization

$V_b = 100.$ mL of $c_b = 0.40$ M of OH^- is combined with $V_a = 100.$ mL of $c_a = 0.40$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = K_w / K_a = 1.0 \times 10^{-8}$ at 25°C.

	$A^-(aq)$	$HA(aq)$	$OH^-(aq)$	Q
Initial	0.20	0	10^{-7}	0
Change	$-x$	$+x$	$+x$	
Equilibrium	$0.20 - x$	x	$10^{-7} + x$	1.0×10^{-8}
Approximate	≈ 0.20	x	$\approx x$	1.0×10^{-8}

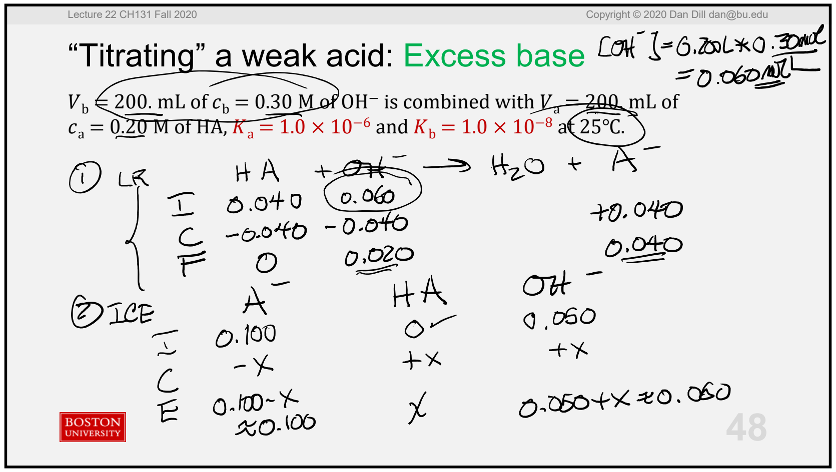
$$[OH^-] = x = (K_b \times [A^-])^{1/2} = (1.0 \times 10^{-8} \times 0.20)^{1/2} = \underline{4.5 \times 10^{-5}}$$

$$[H_3O^+] = K_w / [OH^-] = (1.0 \times 10^{-14}) / (4.5 \times 10^{-5}) = \underline{2.2 \times 10^{-10}}$$

BOSTON UNIVERSITY

47

47



“Titrating” a weak acid: Excess base

$[OH^-] = 0.200 L * 0.30$ mol $= 0.060$ mol

$V_b = 200.$ mL of $c_b = 0.30$ M of OH^- is combined with $V_a = 200.$ mL of $c_a = 0.20$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = 1.0 \times 10^{-8}$ at 25°C.

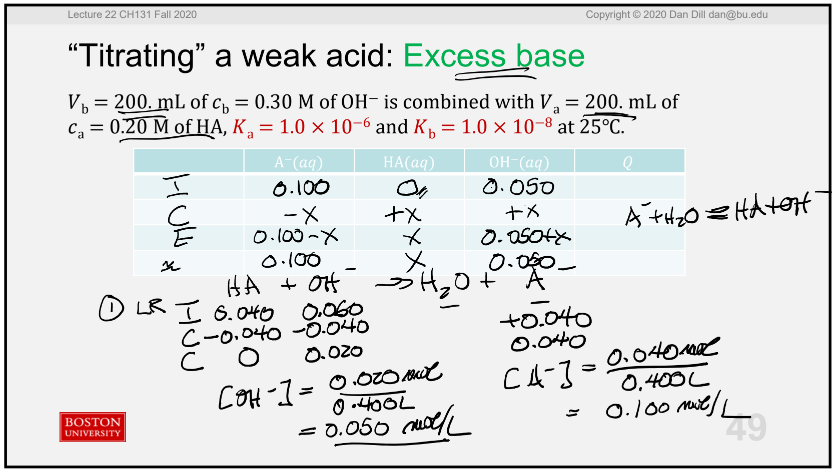
① LR

$HA + \cancel{OH^-} \rightarrow H_2O + A^-$

	HA	OH^-	A^-
I	0.040	0.060	
C	−0.040	−0.040	+0.040
F	0	0.020	0.040

② ICE

	A^-	HA	OH^-
I	0.100	0	0.060
C	−x	+x	+x
E	0.100 − x ≈ 0.100	x	0.050 + x ≈ 0.060



“Titrating” a weak acid: Excess base

$V_b = 200.$ mL of $c_b = 0.30$ M of OH^- is combined with $V_a = 200.$ mL of $c_a = 0.20$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = 1.0 \times 10^{-8}$ at 25°C.

	$A^-(aq)$	$HA(aq)$	$OH^-(aq)$	Q
I	0.100	0	0.050	
C	−x	+x	+x	
E	0.100 − x	x	0.050 + x	
≈	0.100	x	0.050	

$A^- + H_2O \rightleftharpoons HA + OH^-$

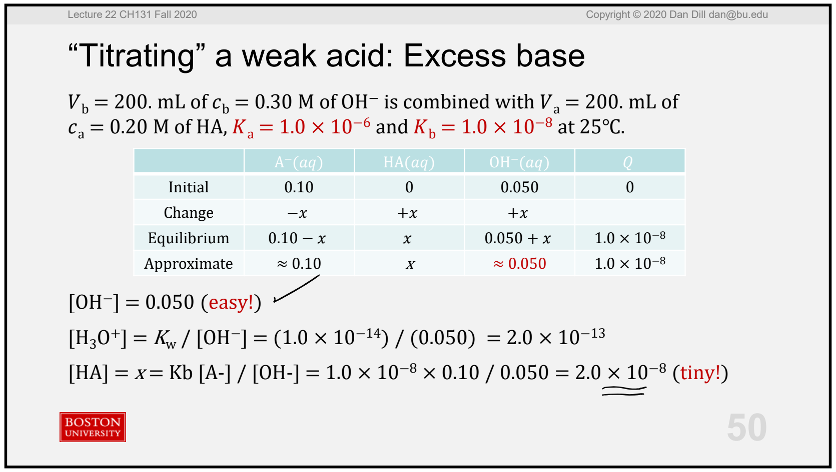
① LR

$HA + OH^- \rightarrow H_2O + A^-$

	HA	OH^-	A^-
I	0.040	0.060	
C	−0.040	−0.040	+0.040
C	0	0.020	0.040

$[OH^-] = \frac{0.020 \text{ mol}}{0.400 L} = 0.050$ mol/L

$[A^-] = \frac{0.040 \text{ mol}}{0.400 L} = 0.100$ mol/L



“Titrating” a weak acid: Excess base

$V_b = 200.$ mL of $c_b = 0.30$ M of OH^- is combined with $V_a = 200.$ mL of $c_a = 0.20$ M of HA, $K_a = 1.0 \times 10^{-6}$ and $K_b = 1.0 \times 10^{-8}$ at 25°C.

	$A^-(aq)$	$HA(aq)$	$OH^-(aq)$	Q
Initial	0.10	0	0.050	0
Change	−x	+x	+x	
Equilibrium	0.10 − x	x	0.050 + x	1.0×10^{-8}
Approximate	≈ 0.10	x	≈ 0.050	1.0×10^{-8}

$[OH^-] = 0.050$ (easy!)

$[H_3O^+] = K_w / [OH^-] = (1.0 \times 10^{-14}) / (0.050) = 2.0 \times 10^{-13}$

$[HA] = x = K_b [A^-] / [OH^-] = 1.0 \times 10^{-8} \times 0.10 / 0.050 = 2.0 \times 10^{-8}$ (tiny!)