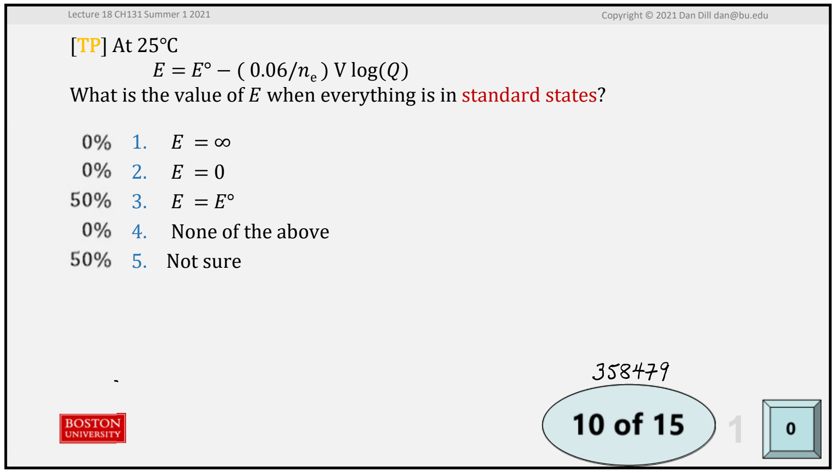

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[TP] At 25°C

$E = E° - (0.06/n_e)\ \mathrm{V}\ \log(Q)$

What is the value of E when everything is in standard states?

0% 1. $E = \infty$

0% 2. $E = 0$

50% 3. $E = E°$

0% 4. None of the above

50% 5. Not sure

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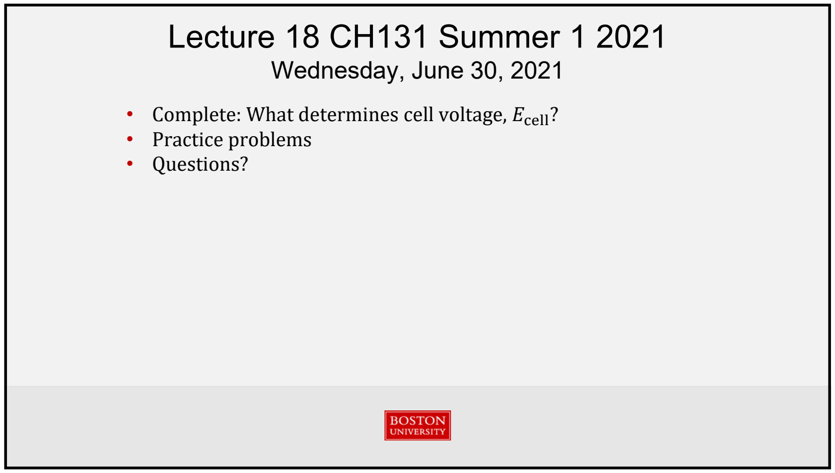
1

0

1

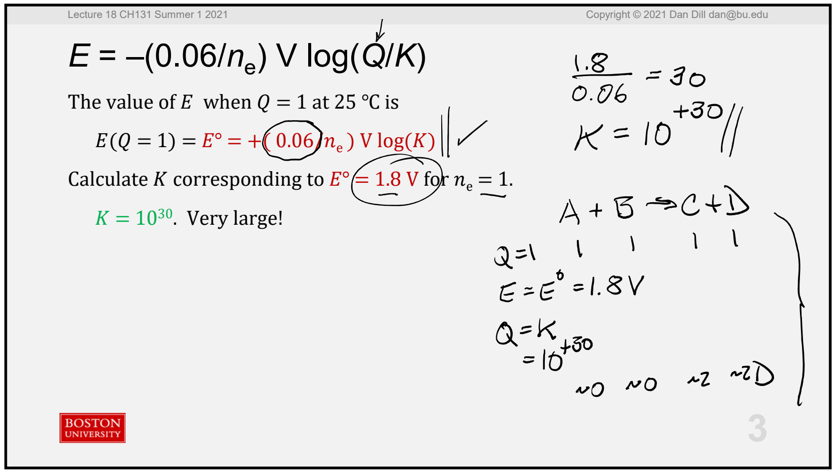


Lecture 18 CH131 Summer 1 2021

Wednesday, June 30, 2021

- Complete: What determines cell voltage, E_{cell}?
- Practice problems
- Questions?

2



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$E = -(0.06/n_e)\ \mathrm{V}\ \log(\overset{\downarrow}{Q}/K)$

The value of E when $Q = 1$ at 25 °C is

$E(Q = 1) = E° = +(\boxed{0.06}/n_e)\ \mathrm{V}\ \log(K)$ || ✓

Calculate K corresponding to $E° = \underline{1.8}\ \mathrm{V}$ for $n_e = \underline{1}$.

$K = 10^{30}$. Very large!

$$\frac{1.8}{0.06} = 30$$

$$K = 10^{+30} \ //$$

$$A + B \rightarrow C + D$$

$Q=1$ 1 1 1 1

$E = E^{0} = 1.8\,\mathrm{V}$

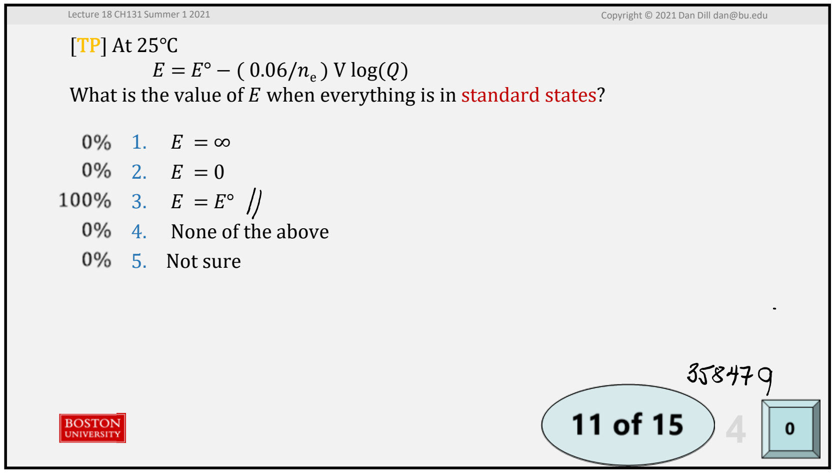
$Q = K$

$= 10^{+30}$

~0 ~0 ~2 ~2D

3

3



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[TP] At 25°C

$E = E° - (0.06/n_e)\ \mathrm{V}\ \log(Q)$

What is the value of E when everything is in standard states?

0% 1. $E = \infty$

0% 2. $E = 0$

100% 3. $E = E°$ //

0% 4. None of the above

0% 5. Not sure

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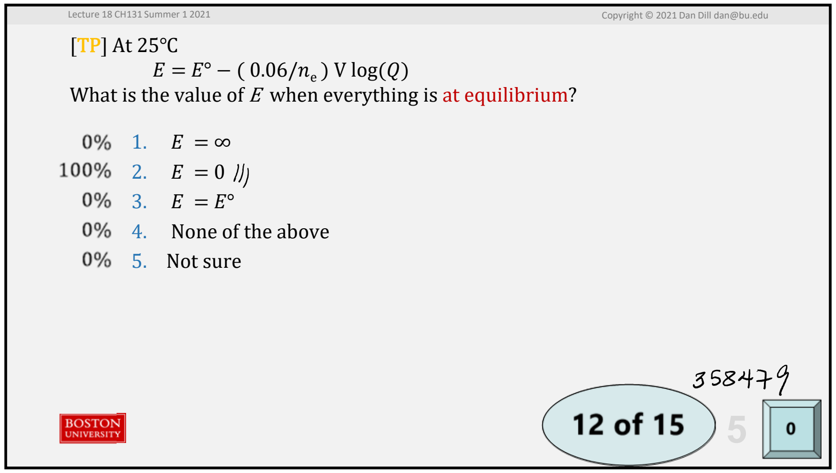
4

0

4



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[TP] At 25°C

$$E = E° − (0.06/n_e)\ \mathrm{V} \log(Q)$$

What is the value of E when everything is at equilibrium?

0%	1. $E = \infty$
100%	2. $E = 0$ ///
0%	3. $E = E°$
0%	4. None of the above
0%	5. Not sure

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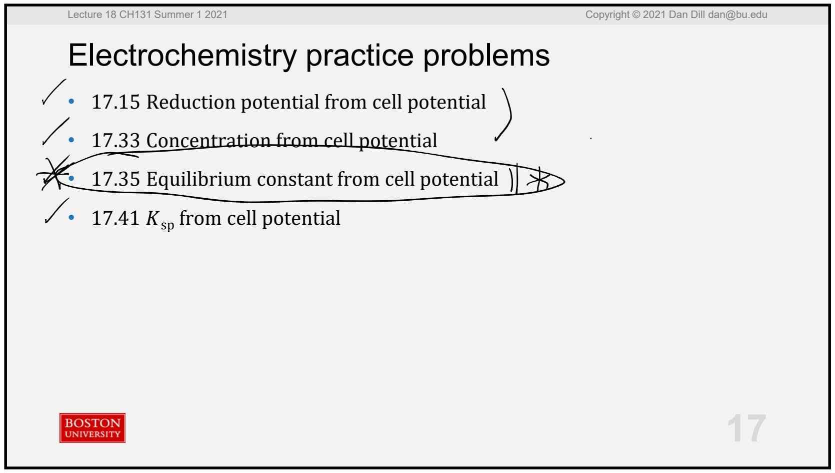
12 of 15 5 0

5



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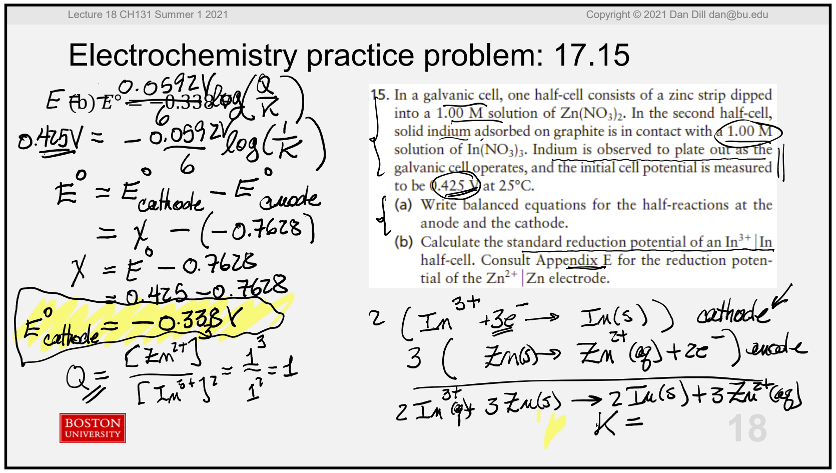
Electrochemistry practice problems

- ✓ 17.15 Reduction potential from cell potential
- ✓ 17.33 Concentration from cell potential
- ✗ 17.35 Equilibrium constant from cell potential ✱
- ✓ 17.41 K_{sp} from cell potential

17

17



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Electrochemistry practice problem: 17.15

15. In a galvanic cell, one half-cell consists of a zinc strip dipped into a 1.00 M solution of $Zn(NO_3)_2$. In the second half-cell, solid indium adsorbed on graphite is in contact with a 1.00 M solution of $In(NO_3)_3$. Indium is observed to plate out as the galvanic cell operates, and the initial cell potential is measured to be 0.425 V at 25°C.
    (a) Write balanced equations for the half-reactions at the anode and the cathode.
    (b) Calculate the standard reduction potential of an $In^{3+}|In$ half-cell. Consult Appendix E for the reduction potential of the $Zn^{2+}|Zn$ electrode.

$$E\ \text{(b)}\ E° = \cancel{-0.338}\ \frac{0.0592\,V}{6}\log\left(\frac{Q}{K}\right)$$

$$0.425V = -\frac{0.0592V}{6}\log\left(\frac{1}{K}\right)$$

$$E° = E°_{cathode} - E°_{anode}$$

$$= x - (-0.7628)$$

$$x = E° - 0.7628$$

$$= 0.425 - 0.7628$$

$$\boxed{E°_{cathode} = -0.338V}$$

$$Q = \frac{[Zn^{2+}]^3}{[In^{3+}]^2} = \frac{1^3}{1^2} = 1$$

$$2\ (In^{3+} + 3e^- \rightarrow In(s))\ \text{cathode}$$

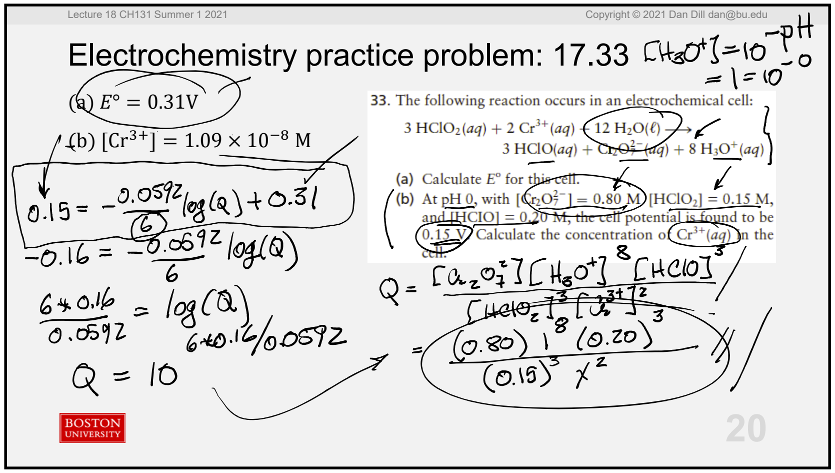
$$3\ (Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-)\ \text{anode}$$

$$2In^{3+}(aq) + 3Zn(s) \rightarrow 2In(s) + 3Zn^{2+}(aq)$$

$$K =$$

18

18



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Electrochemistry practice problem: 17.33

$$[H_3O^+] = 10^{-pH} = 10^{-0} = 1$$

(a) $E° = 0.31V$

(b) $[Cr^{3+}] = 1.09 \times 10^{-8}$ M

33. The following reaction occurs in an electrochemical cell:

$$3\,HClO_2(aq) + 2\,Cr^{3+}(aq) + 12\,H_2O(\ell) \longrightarrow 3\,HClO(aq) + Cr_2O_7^{2-}(aq) + 8\,H_3O^+(aq)$$

(a) Calculate $E°$ for this cell.
(b) At pH 0, with $[Cr_2O_7^{2-}] = 0.80$ M, $[HClO_2] = 0.15$ M, and $[HClO] = 0.20$ M, the cell potential is found to be 0.15 V. Calculate the concentration of $Cr^{3+}(aq)$ in the cell.

$$\boxed{0.15 = -\frac{0.0592}{6}\log(Q) + 0.31}$$

$$-0.16 = -\frac{0.0592}{6}\log(Q)$$

$$\frac{6 * 0.16}{0.0592} = \log(Q)$$

$$6*0.16/0.0592$$

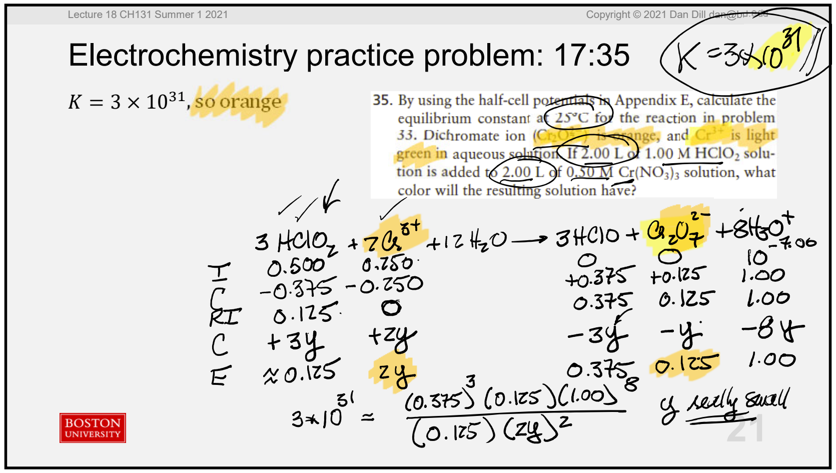
$$Q = 10$$

$$Q = \frac{[Cr_2O_7^{2-}][H_3O^+]^8[HClO]^3}{[HClO_2]^3[Cr^{3+}]^2}$$

$$= \frac{(0.80)\,1^8\,(0.20)^3}{(0.15)^3\,x^2}$$

20

20



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Electrochemistry practice problem: 17:35

$K = 3 \times 10^{31}$

$K = 3 \times 10^{31}$, so orange

35. By using the half-cell potentials in Appendix E, calculate the equilibrium constant at 25°C for the reaction in problem 33. Dichromate ion ($Cr_2O_7^{2-}$) is orange, and Cr^{3+} is light green in aqueous solution. If 2.00 L of 1.00 M $HClO_2$ solution is added to 2.00 L of 0.50 M $Cr(NO_3)_3$ solution, what color will the resulting solution have?

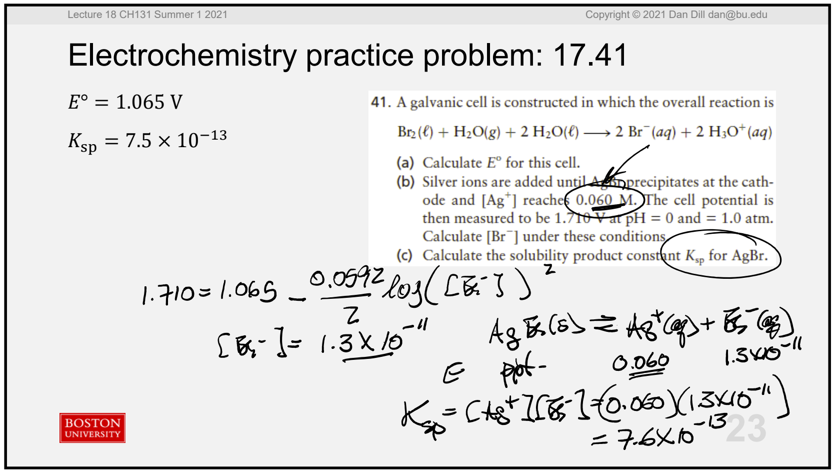
$3\,HClO_2 + 2\,Cr^{3+} + 12\,H_2O \longrightarrow 3\,HClO + Cr_2O_7^{2-} + 8\,H_3O^+$

I	0.500	0.250	0	0	$10^{-7.00}$
C	−0.375	−0.250	+0.375	+0.125	1.00
RI	0.125	0	0.375	0.125	1.00
C	+3y	+2y	−3y	−y	−8y
E	≈0.125	2y	0.375	0.125	1.00

$$3 \times 10^{31} = \frac{(0.375)^3 (0.125)(1.00)^8}{(0.125)(2y)^2}$$

y really small

21



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Electrochemistry practice problem: 17.41

$E° = 1.065\ V$

$K_{sp} = 7.5 \times 10^{-13}$

41. A galvanic cell is constructed in which the overall reaction is

$Br_2(\ell) + H_2O(g) + 2\,H_2O(\ell) \longrightarrow 2\,Br^-(aq) + 2\,H_3O^+(aq)$

(a) Calculate $E°$ for this cell.

(b) Silver ions are added until AgBr precipitates at the cathode and $[Ag^+]$ reaches 0.060 M. The cell potential is then measured to be 1.710 V at pH = 0 and = 1.0 atm. Calculate $[Br^-]$ under these conditions.

(c) Calculate the solubility product constant K_{sp} for AgBr.

$$1.710 = 1.065 - \frac{0.0592}{2}\log([Br^-])^2$$

$[Br^-] = 1.3 \times 10^{-11}$

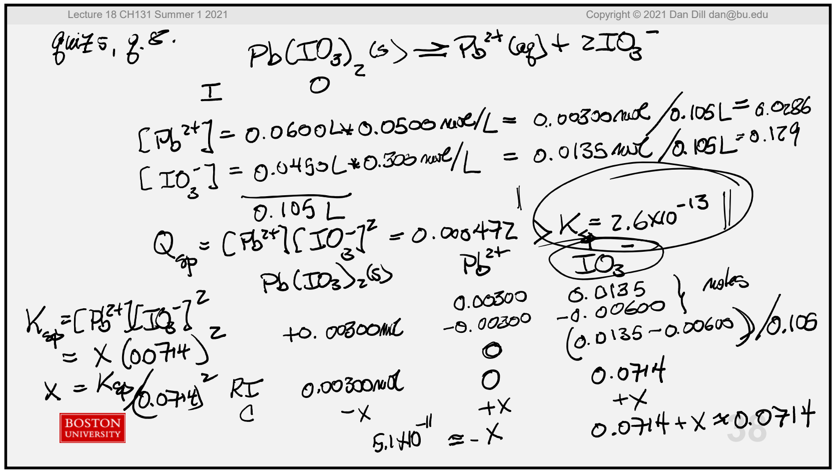
$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

E ppt- 0.060 1.3×10^{-11}

$K_{sp} = [Ag^+][Br^-] = (0.060)(1.3 \times 10^{-11})$

$= 7.6 \times 10^{-13}$

23



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quiz 5, q. 8.

$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,IO_3^-$

I 0

$[Pb^{2+}] = 0.0600\,L * 0.0500\,mol/L = 0.00300\,mol / 0.105\,L = 0.0286$

$[IO_3^-] = \dfrac{0.0450\,L * 0.300\,mol/L}{0.105\,L} = 0.0135\,mol / 0.105\,L = 0.129$

$Q_{sp} = [Pb^{2+}][IO_3^-]^2 = 0.000472 > K_{sp} = 2.6 \times 10^{-13}$

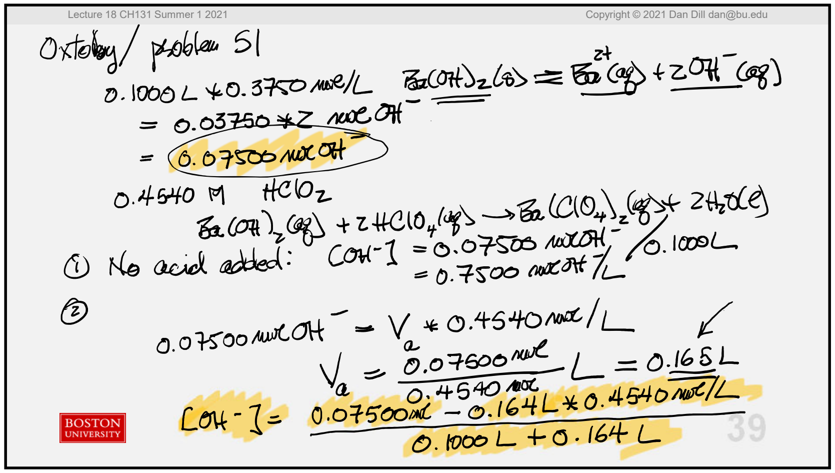
$Pb(IO_3)_2(s)$	Pb^{2+}	IO_3^-
	0.00300	0.0135 } moles
+0.00300 mol	−0.00300	−0.00600
	0	(0.0135 − 0.00600)/0.105
RI 0.00300 mol	0	0.0714
C −x	+x	+x
	$5.1 \times 10^{-11} \approx -x$	$0.0714 + x \approx 0.0714$

$K_{sp} = [Pb^{2+}][IO_3^-]^2$

$= x(00714)^2$

$x = K_{sp}/(0.0714)^2$

38



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Oxtoby / problem 51

$0.1000\,L * 0.3750\,mol/L$ $Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,OH^-(aq)$

$= 0.03750 * 2\ mol\ OH^-$

$= 0.07500\ mol\ OH^-$

0.4540 M $HClO_2$

$Ba(OH)_2(aq) + 2\,HClO_4(aq) \longrightarrow Ba(ClO_4)_2(aq) + 2\,H_2O(\ell)$

① No acid added: $[OH^-] = 0.07500\ mol\ OH^- / 0.1000\,L$

$= 0.7500\ mol\ OH^-/L$

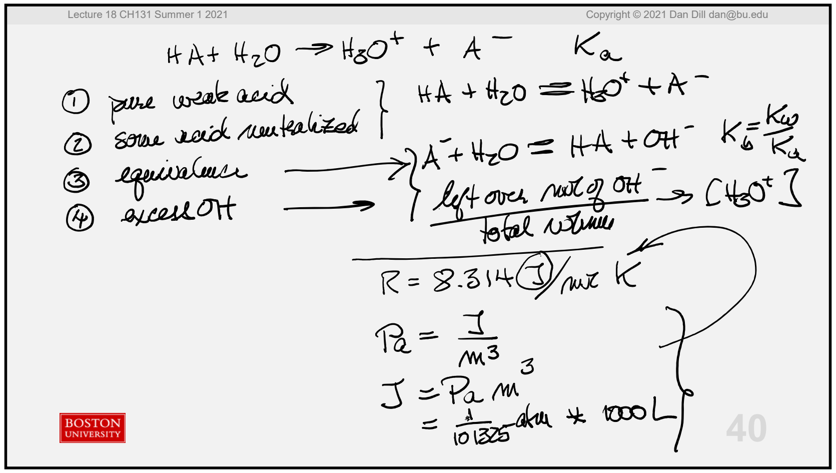
②

$0.07500\ mol\ OH^- = V_a * 0.4540\ mol/L$

$V_a = \dfrac{0.07500\ mol}{0.4540\ mol}\,L = 0.165\,L$

$$[OH^-] = \frac{0.07500\ mol - 0.164\,L * 0.4540\ mol/L}{0.1000\,L + 0.164\,L}$$

39



$HA + H_2O \rightarrow H_3O^+ + A^-$ K_a

① pure weak acid

② some acid neutralized

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

③ equivalence $\rightarrow$ $A^- + H_2O \rightleftharpoons HA + OH^-$ $K_b = \frac{K_w}{K_a}$

④ excess OH $\rightarrow$ $\frac{\text{left over mol of } OH^-}{\text{total volume}} \rightarrow [H_3O^+]$

$R = 8.314\,\boxed{J}/\text{mol K}$

$Pa = \frac{J}{m^3}$

$J = Pa\, m^3$

$= \frac{1}{101325}\,\text{atm} * 1000\,L$

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