Chapter 8 Homework Solutions

8.1   **(a)** $n(H^+) = 0.144$ mol/L x 0.025 L $= 3.60 \times 10^{-3}$ mol

$n(OH^-) = 0.125$ mol/L x 0.025 L $= 3.12 \times 10^{-3}$ mol

After neutralization, excess $n(H^+) = 3.6 \times 10^{-3}$ mol $- 3.12 \times 10^{-3}$ mol $= 4.8 \times 10^{-4}$ mol

$$[H^+] = \frac{n(H^+)}{V} = \frac{4.8 x 10^{-4}\ mol}{(0.025 + 0.025)\,L} = 9.6 x 10^{-3}\ M$$

pH $= -\log([H^+]) = -\log(9.6 \times 10^{-3}$ M$) = 2.02$

(b) $n(H^+) = 0.15$ mol/L x 0.025 L $= 3.75 \times 10^{-3}$ mol

$n(OH^-) = 0.15$ mol/L x 0.035 L $= 5.25 \times 10^{-3}$ mol

After neutralization, excess $n(OH^-) = 5.25 \times 10^{-3}$ mol $- 3.75 \times 10^{-3}$ mol $= 1.50 \times 10^{-3}$ mol

$$[OH^-] = \frac{n(OH^-)}{V} = \frac{1.50 x 10^{-3}\ mol}{(0.025 + 0.035)\,L} = 2.5 x 10^{-2}\ M$$

$$[H^+] = \frac{1 x 10^{-14}}{[OH^-]} = \frac{1 x 10^{-14}}{2.5 x 10^{-2}\ M} = 4.0 x 10^{-13}\ M$$

pOH $= -\log([OH^-]) = -\log(2.5 \times 10^{-2}$ M$) = 1.60$

pH $= 14.0 - $ pOH $= 14.0 - 1.60 = 12.40$

(c) $n(H^+) = 0.22$ mol/L x 0.0212 L $= 4.66 \times 10^{-3}$ mol

$n(OH^-) = 0.30$ mol/L x 0.010 L $= 3.00 \times 10^{-3}$ mol

After neutralization, excess $n(H^+) = 4.66 \times 10^{-3}$ mol $- 3.00 \times 10^{-3}$ mol $= 1.66 \times 10^{-3}$ mol

$$[H^+] = \frac{n(H^+)}{V} = \frac{1.66 x 10^{-3}\ mol}{(0.0212 + 0.010)\,L} = 5.32 x 10^{-2}\ M$$

pH $= -\log([H^+]) = -\log(5.32 \times 10^{-2}$ M$) = 1.2$

8.2   **(a)** Calculate the molar concentration of $KC_2H_3O_2$

$$(8.4\ g) \times \left(\frac{1\ mol}{98.1\ g}\right) \times \left(\frac{1}{0.250\ L}\right) = 0.342\ mol\ L^{-1}$$

	$H_2O(l)$ + Lac^-(aq)	f	HAc(aq) +	OH^-(aq)
Initial	— 0.342		0	0
Change	— $-x$		$+x$	$+x$
Equilibrium	— $0.342 - x \cong 0.342$		x	x

$$K_b = \frac{1.0x10^{-14}}{1.8x10^{-5}} = 5.6x10^{-10} = \frac{x \cdot x}{0.342 - x} \approx \frac{x^2}{0.342}$$

$x^2 = 1.92x10^{-10} \rightarrow x = [OH^-] = 1.38x10^{-5}$

$pOH = -log([OH^-]) = -log(1.38x10^{-5}) = 4.86$

$pH = 14.00 - 4.86 = 9.14$

(b) $(3.75 \text{ g}) \times \left(\frac{1 \text{ mol}}{97.9 \text{ g}}\right) \times \left(\frac{1}{0.100 \text{ L}}\right) = 0.383 \text{ mol L}^{-1} \text{ NH}_4\text{Br}$

$NH_4^+(aq) \quad + \quad H_2O(l) \; Ё \; NH_3(aq) \quad + \quad H_3O^+(aq)$			
Initial	0.383	—	0	0
Change	$-x$	—	$+x$	$+x$
Equilibrium	$0.383 - x \cong 0.383$	—	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0x10^{-14}}{1.8x10^{-5}} = 5.6x10^{-10} = \frac{x \cdot x}{0.383 - x} \approx \frac{x^2}{0.383}$$

$x^2 = 2.14x10^{-10} \rightarrow x = [H^+] = 1.46x10^{-5}$

$pH = -log([H^+]) = -log(1.46x10^{-5}) = 4.83$

8.3 **(a)** $HLac = H^+ + Lac^- \quad K_a = 8.4x10^{-4} \quad [HLac] = 0.1 - x \qquad [H^+] = [Lac^-] = x$

$$K_a = 8.4x10^{-4} = \frac{x \cdot x}{0.1 - x} \approx \frac{x^2}{0.1} \rightarrow x^2 = 8.4x10^{-5} \rightarrow x = [H^+] = 9.2x10^{-3} \text{ M}$$

$pH = -log([H^+]) = -log(9.2x10^{-3}) = 2.04$

(b) $Lac^- + H_2O = HLac + OH^- \quad K_b = 10^{-14}/8.4x10^{-4} = 1.2x10^{-11}$
$$[Lac^-] = 2.0 - x \quad [HLac] = [OH^-] = x$$
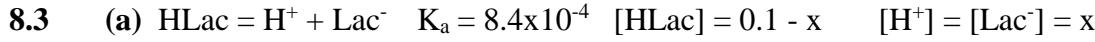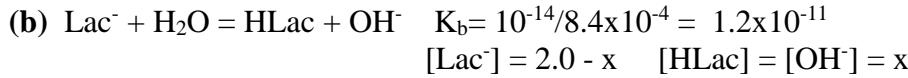
$$K_b = 1.2x10^{-11} = \frac{x \cdot x}{2.0 - x} \approx \frac{x^2}{2.0} \rightarrow x^2 = 2.4x10^{-11} \rightarrow x = [OH^-] = 4.9x10^{-6}$$

$pOH = -log([OH^-]) = -log(4.9x10^{-6}) = 5.3 \quad pH = 14.0 - pOH = 14.0 - 5.3 = 8.7$

(c) **Initial:** $(n_{HLac})_{init} = 0.1 \text{ mol/L} \times 0.20 \text{ L} = 0.02 \text{ mol} \quad (n_{Lac-})_{init} = 0.0$

$(n_{OH^-}) = 0.05 \text{ mol/L} \times 0.10 \text{ L} = 0.005 \text{ mol}$

$HLac + OH^- \rightarrow Lac^- + H_2O$
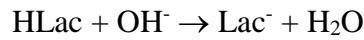
$$V = 0.20 \text{ L} + 0.1 \text{ L} = 0.30 \text{ L}$$

Final: $(n_{Hlac})_{fin} = 0.02 - 0.005 = 0.015 \text{ mol}$ $(n_{Lac-})_{fin} = 0.0 + 0.005 = 0.005 \text{ mol}$

$[HLac]_{fin} = 0.015 \text{ mol}/0.30 \text{ L} = 0.050 \text{ M}$ $[Lac^-]_{fin} = 0.005 \text{ mol}/0.30 \text{ L} = 0.0167 \text{ M}$

$pKa = -\log(8.4 \times 10^{-4}) = 3.08$

$$pH = pK_a + \log\left\{\frac{[Lac^-]}{[HLac]}\right\} = 3.08 + \log\left\{\frac{0.0167}{0.050}\right\} = 3.08 - 0.48 = 2.60$$

8.4 **(a)** $Anil + H_2O \rightleftharpoons AnilH^+ + H_2O$ $K_b = 4.3 \times 10^{-10}$ $[Anil] = 0.05 - x$ $[AnilH^+] = [OH^-] = x$
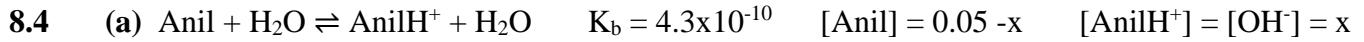
$$K_b = 4.3 \times 10^{-10} = \frac{x \cdot x}{0.05 - x} \approx \frac{x^2}{0.05} \rightarrow x^2 = 2.15 \times 10^{-11} \rightarrow x = [OH^-] = 4.64 \times 10^{-6} \text{ M}$$

$pOH = -\log([OH^-]) = -\log(4.64 \times 10^{-3}) = 5.33$ $pH = 14.0 - pOH = 8.67$

(b) $AnilH^+ = Anil + H^+$ $K_a = 1 \times 10^{-14}/K_b = 2.3 \times 10^{-5}$

$$[AnilH^+] = 0.10 - x \quad [Anil] = [H^+] = x$$

$$K_b = 2.3 \times 10^{-5} = \frac{x \cdot x}{0.10 - x} \approx \frac{x^2}{0.10} \rightarrow x^2 = 2.3 \times 10^{-6} \rightarrow x = [H^+] = 1.51 \times 10^{-3}$$

$pH = -\log([H^+]) = -\log(1.51 \times 10^{-3}) = 2.82$

(c) **Initial:** $(n_{Anil})_{init} = 0.05 \text{ mol/L} \times 0.40 \text{ L} = 0.02 \text{ mol}$ $(n_{AnilH^+})_{init} = 0$

$n_{H^+} = 0.15 \text{ mol/L} \times 0.10 \text{ L} = 0.015 \text{ mol}$

$V = 0.40 \text{ L} + 0.10 \text{ L} = 0.50 \text{ L}$

$Anil + H^+ \rightarrow AnilH^+$
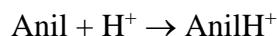
Final: $(n_{Anil})_{fin} = 0.02 - 0.015 = 0.005 \text{ mol}$ $(n_{AnilH+})_{fin} = 0.0 + 0.015 = 0.015 \text{ mol}$

$[Anil]_{fin} = 0.005 \text{ mol}/0.50 \text{ L} = 0.010 \text{ M}$ $[AnilH^+]_{fin} = 0.015 \text{ mol}/0.50 \text{ L} = 0.030 \text{ M}$

$pKb = -\log(4.3 \times 10^{-10}) = 9.36$ $pKa = 14 - 9.36 = 4.64$

$$pH = pK_a + \log\left\{\frac{[Anil]}{[AnilH^+]}\right\} = 4.64 + \log\left\{\frac{0.010}{0.030}\right\} = 4.64 - 0.48 = 4.16$$

8.5   For each of the solutions below, indicate whether the solution would be a buffer.

a) YES: $n(HAc) = 1.0$ mol , $n(OH^-) = 0.50$ mol. OH^- converts part of HAc to Ac^-

b) YES: $n(Ac^-) = 1.6$ mol , $n(H^+) = 1.0$ mol. H^+ converts part of Ac^- to HAc

c) NO: H_2CO_3 and CO_3^{2-} are not a conjugate acid/conjugate base of each other

d) YES: $n(CO_3^{2-}) = 1.0$ mol , $n(H^+) = 0.50$ mol. H^+ converts part of CO_3^{2-} to HCO_3^-

e) YES: $n(CO_3^{2-}) = 1.0$ mol , $n(H^+) = 1.50$ mol. H^+ converts all CO_3^{2-} to HCO_3^- and then converts part of HCO_3^- to H_2CO_3

f) NO: $n(CO_3^{2-}) = 1.0$ mol , $n(H^+) = 2.50$ mol. H^+ converts all CO_3^{2-} to HCO_3^-, and then to H_2CO_3 (and there is even H^+ left over). We do not have an acid/base conjugate pair at the end of the reaction.

8.6   The following independent questions are on pH calculations in solutions of Arsenic Acid (H_3AsO_4) and its various anions. H_3AsO_4 is a triprotic acid with Acid Dissociation Constants:
$K_a' = 6.0 \times 10^{-3}$, $K_a'' = 1.0 \times 10^{-7}$, $K_a''' = 3.2 \times 10^{-12}$

$$H_3AsO_4 \xrightleftharpoons[pKa'=2.22]{Ka'=6.0 \times 10^{-3}} H_2AsO_4^- \xrightleftharpoons[pKa'=7.00]{Ka''=1.0 \times 10^{-7}} HAsO_4^{2-} \xrightleftharpoons[pKa'=11.49]{Ka''=3.2 \times 10^{-12}}$$
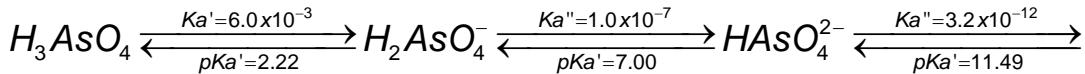
a) $n(H3AsO4) = 1.2$ mol , $n(OH-) = 0.8$ mol
1st. (only) Reaction: H3AsO4 + OH- → H2AsO4-

	H3AsO4	OH-	H2AsO4-
Initial	1.2	0.8	0
Change	-0.8	-0.8	+0.8
Final	0.4	0	0.8
Conc	0.10	0	0.20

$$pH = pK_a' + \log\left(\frac{[H2AsO4\text{-}]}{[H3AsO4]}\right) = 2.22 + \log\left(\frac{0.20}{0.10}\right) = 2.22 + 0.30 = 2.52$$

b) $n(H3AsO4) = 1.2$ mol , $n(OH-) = 1.6$ mol
1st. Reaction: H3AsO4 + OH- → H2AsO4-

	H3AsO4	OH-	H2AsO4-
Initial	1.2	1.6	0
Change	-1.2	-1.2	+1.2
Final	0	0.4	1.2
Conc		0	

2nd. Reaction: H2AsO4- + OH- → HAsO4-2

	H2AsO4-	OH-	HAsO4-2
Initial	1.2	0.4	0
Change	-0.4	-0.4	+0.4
Final	0.8	0	0.4
Conc	0.16	0	0.08

$$pH = pK_a'' + \log\left(\frac{[HAsO4-2]}{[H2AsO4-]}\right) = 7.00 + \log\left(\frac{0.08}{0.16}\right) = 7.00 + (-0.30) = 6.70$$

c) $n(AsO4-3) = 1.2$ mol , $n(H+) = 0.8$ mol
1st. (only) Reaction: AsO4-3 + H+ → HAsO4-2

	AsO4-3	H+	HAsO4-2
Initial	1.2	0.8	0
Change	-0.8	-0.8	+0.8
Final	0.4	0	0.8
Conc	0.10	0	0.20

$$pH = pK_a''' + \log\left(\frac{[AsO4-3]}{[HAsO4-2]}\right) = 11.49 + \log\left(\frac{0.10}{0.20}\right) = 11.49 + (-0.30) = 11.19$$

c) $n(AsO4-3) = 1.2$ mol , $n(H+) = 1.6$ mol
1st. Reaction: AsO4-3 + H+ → AsO4-2

	AsO4-3	H+	HAsO4-2
Initial	1.2	1.6	0
Change	-1.2	-1.2	+1.2
Final	0	0.4	1.2
Conc			

2nd. Reaction: HAsO4-2 + H+ → H2AsO4-

	HAsO4-2	H+	H2AsO4-
Initial	1.2	0.4	0
Change	-0.4	-0.4	+0.4
Final	0.8	0	0.4
Conc	0.16	0	0.08

$$pH = pK_a'' + \log\left(\frac{[HAsO4 - 2]}{[H2AsO4-]}\right) = 7.00 + \log\left(\frac{0.16}{0.08}\right) = 7.00 + (0.30) = 7.30$$

e) $$pH = pK_a'' + \log\left(\frac{[HAsO4^{-2}]}{[H_2AsO4^-]}\right) = 7.00 + \log(1.50) = 7.00 + (0.18) = 7.18$$

f) $[AsO_4^{-3}]/[HSO_4^{-2}] = 1/2.50 = 0.40$

$$pH = pK_a''' + \log\left(\frac{[AsO4^{-3}]}{[HAsO4^{-2}]}\right) = 11.49 + \log(0.40) = 11.49 + (-0.40) = 11.09$$

g) $$pH = 2.60 = pK_a' + \log\left(\frac{[H2AsO4-]}{[H3AsO4]}\right) = 2.22 + \log\left(\frac{[H2AsO4-]}{[H3AsO4]}\right)$$

$$\log\left(\frac{[H2AsO4-]}{[H3AsO4]}\right) = 2.60 - 2.22 = 0.38 \rightarrow \frac{[H2AsO4-]}{[H3AsO4]} = 10^{0.38} = 2.40$$

h) $$pH = 10.90 = pK_a''' + \log\left(\frac{[AsO4 - 3]}{[HAsO4 - 2]}\right) = 11.49 + l\log\left(\frac{[AsO4 - 3]}{[HAsO4 - 2]}\right)$$

$$\log\left(\frac{[AsO4 - 3]}{[HAsO4 - 2]}\right) = 10.90 - 11.49 = -0.59 \rightarrow \frac{[AsO4 - 3]}{[HAsO4 - 2]} = 10^{-0.59} = 0.257$$

$$\frac{[HAsO4 - 2]}{[AsO4 - 3]} = \frac{1}{0.257} = 3.89 \approx 3.9$$

8.7 $HCOOH = H^+ + HCOO^-$ $K_a = 1.8 \times 10^{-4}$ $pKa = -\log(1.8 \times 10^{-4}) = 3.74$

$$pH = 4.25 = pK_a + \log\left\{\frac{[HCOO^-]}{[HCOOH]}\right\} = 3.74 + \log\left\{\frac{[HCOO^-]}{[HCOOH]}\right\}$$

$$\log\left\{\frac{[HCOO^-]}{[HCOOH]}\right\} = 0.51 \rightarrow \frac{[HCOO^-]}{[HCOOH]} = 10^{0.51} = 3.24 \rightarrow [HCOO^-] = 3.24[HCOOH] \text{ (Eqn. 1)}$$

$[HCOOH] + [HCOO^-] = [HCOOH\}_{init} = 0.50 \text{ M (Eqn. 1)}$

Therefore: $[HCOOH] + 3.24[HCOOH] = 0.50$

$4.24[HCOOH] = 0.50$

$[HCOOH] = 0.50/4.24 = 0.12 \text{ M}$

$$[HCOO^-] = 0.50 - 0.12 = 0.38 \text{ M}$$

8.8   Addition of Strong Base to HBenz: HBenz + NaOH $\rightarrow$ Na$^+$ + Benz$^-$ + H$_2$O

Initial: $(n_{HBenz})_{init} = M_{HBenz} \text{ x } V_{HBenz} = 0.40 \text{ mol/L x } 0.50 \text{ L} = 0.20 \text{ mol}$

(a) Number of mL of NaOH needed to reach half-way to equiv. point

Need $n_{NaOH} = (1/2) \text{ x } 0.20 \text{ mol} = 0.10 \text{ mol}$

$$V_{NaOH} = \frac{n_{NaoH}}{M_{NaoH}} = \frac{0.10 \, mol}{1.0 \, mol/L} = 0.10 \, L = 100 \, mL$$

pH Half-way to equivalence point, [Benz$^-$] = [HBenz]

$$pKa = -\log(Ka) = -\log(6.5 \text{x} 10^{-5}) = 4.19$$

$$pH = pK_a + \log\left\{\frac{[Benz^-]}{[HBenz]}\right\} = pK_a + \log(1) = pK_a = 4.19$$

(b) Number of mL of NaOH needed to reach the equiv. point

Need $n_{NaOH} = 0.20 \text{ mol}$

$$V_{NaOH} = \frac{n_{NaOH}}{M_{NaOH}} = \frac{0.20 \, mol}{1.0 \, mol/L}$$

pH at equivalence point. Have 100% Benz$^-$ (the benzoate ion)

This is a pure base with $K_b = 10^{-14}/Ka = 10^{-14}/6.5 \text{x} 10^{-5} = 1.5 \text{x} 10^{-10}$

$$[Benz^-] = \frac{0.20 \, mol}{0.50 \, L + 0.20 \, L} = 0.29 \, M$$

It will react with water according to the equation: Benz$^-$ + H$_2$O $\rightleftarrows$ HBenz + OH$^-$

$$K_b = \frac{[HBenz][OH^-]}{[Benz^-]} = \frac{x \bullet x}{0.29} = 1.5 x 10^{-10}$$

$$x = [OH^-] = \sqrt{(0.29(1.5 x 10^{-10})} = 6.6 x 10^{-6} \, M$$

$$pOH = -\log(6.6 x 10^{-6}) = 5.2$$

$$pH = 14 - 5.2 = 8.8$$

8.9 $pK_a^{'} = 2.35 \quad pK_a^{''} = 9.69$

$Ala^+ \quad \leftrightarrow \quad Ala \quad \leftrightarrow \quad Ala^-$

(a) $\dfrac{[Ala^+]}{[Ala]} = 0.25 \rightarrow \dfrac{[Ala]}{[Ala^+]} = 4.0$

$$pH = pKa' + \log\left\{\dfrac{[Ala]}{[Ala^+]}\right\} = 2.35 + \log(4.0) = 2.35 + 0.60 = 2.95$$

(b) $pH = pK_a^{''} + \log\left\{\dfrac{[Ala^-]}{[Ala]}\right\} \rightarrow \log\left\{\dfrac{[Ala^-]}{[Ala]}\right\} = pH - pK_a^{''} = 10.5 - 9.69 = 0.81$

$$\dfrac{[Ala^-]}{[Ala]} = 10^{0.81} = 6.5$$

(c)   We have a solution containing [Ala$^+$] and [Ala]. [Ala$^+$] + [Ala] = 0.80 M

$$pH = 2.00 = pK_a^{'} + \log\left\{\dfrac{[Ala]}{[Ala^+]}\right\} = 2.35 + \log\left\{\dfrac{[Ala]}{[Ala^+]}\right\}$$

$$\log\left\{\dfrac{[Ala]}{[Ala^+]}\right\} = 2.00 - 2.35 = -0.35$$

$$\dfrac{[Ala]}{[Ala^+]} = 10^{-0.35} = 0.45 \rightarrow [Ala] = 0.45[Ala^+]$$

0.80 M = [Ala$^+$] + [Ala] = [Ala$^+$] + 0.45[Ala$^+$] = 1.45[Ala$^+$]

$$[Ala^+] = \dfrac{[0.80]}{1.45} = 0.55\,M \text{ and } [Ala] = 0.80 - .55 = 0.25 \text{ M}$$

8.10 $pK_a^{'} = 2.18 \quad pK_a^{''} = 8.95 \quad pK_a^{'''} = 10.53$
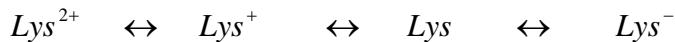
$Lys^{2+} \quad \leftrightarrow \quad Lys^+ \quad \leftrightarrow \quad Lys \quad \leftrightarrow \quad Lys^-$

(a) After adding 0.5 equiv., [Lys$^+$] = [Lys^{2+}]

$$pH = pK_a^{'} + \log\left\{\dfrac{[Lys^+]}{[Lys^{2+}]}\right\} = 2.18 + \log(1) = 2.18 \qquad \text{Avg. Charge} = +1.5$$

(b) After adding 1.0 equiv., have pure Lys$^+$

$$pH = \dfrac{1}{2}\left(pK_a^{'} + pK_a^{''}\right) = \dfrac{1}{2}(2.18 + 8.95) = 5.57 \qquad \text{Avg. Charge} = +1.0$$

(c) At the isoelectric point, pI, have pure Lys (with Avg. Charge = 0.0)

$$pI = \frac{1}{2}\left(pK_a'' + pK_a'''\right) = \frac{1}{2}(8.95 + 10.53) = 9.74$$

(d) At pH = 10.53, pH = pKa'''. Therefore, [Lys⁻] = [Lys]

This requires adding 2.5 equivalents.

(e) After adding 2.5 equiv. of NaOH to the protonated form, the solution contains 50% [Lys] and 50% [Lys⁻]. Therefore, the average charge is -1/2 .

8.11 $MgF_2(s) = Mg^{2+}(aq) + 2\ F^-(aq)$ $K_s = 6.4 \times 10^{-9} = [Mg^{2+}][F^-]^2$
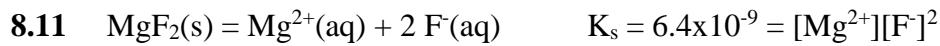
(a) $[Mg^{2+}] = s$ $[F^-] = 2s$

$K_s = 6.4 \times 10^{-9} = s(2s)^2 = 4s^3 \rightarrow s^3 = 1.6 \times 10^{-9} \rightarrow s = 1.17 \times 10^{-3}$

(b) $[Mg^{2+}] = 0.1 + s \approx 0.1$ $[F^-] = 2s$

$K_s = 6.4 \times 10^{-9} = (0.1)(2s)^2 = 0.4s^2 \rightarrow s^2 = 1.6 \times 10^{-8} \rightarrow s = 1.26 \times 10^{-4}$

(c) $[Mg^{2+}] = s$ $[F^-] = 0.2 + 2s \approx 0.2$

$K_s = 6.4 \times 10^{-9} = (s)(0.2)^2 = 0.04s \rightarrow s = 1.6 \times 10^{-7}$