Aqueous Equilibrium Test Review Key

1. Common Ion Effect

(A) What does having a common ion in a solution do to equilibrium and why?

The common ion lowers the solubility of the compound in solution because equilibrium shifts to the left (toward the solid and away from the ions in solution).

(B) Calculate the pH of a mixture of 0.100M $HC_3H_5O_2$ and 0.080M $NaC_3H_5O_2$. $K_a = 1.3 \times 10^{-5}$

$$HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^-$$

.100M ? .080M

$$K_a = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]}$$

$$1.3\times10^{-5} = \frac{[H^+][.080]}{[.100]}$$

$$[H^+] = 1.63\times10^{-5}\ M$$

$$pH = -\log[H^+] = -\log[1.63\times10^{-5}]$$

$$pH = 4.79$$

(C) Calculate the pH of a mixture of 0.100M $HONH_2$ (base) and 0.0750M $HONH_3^+$ (acid). $K_b = 1.1 \times 10^{-8}$

$$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$$

.100M .0750M ?

$$K_b = \frac{[HONH_3^+][OH^-]}{[HONH_2]}$$

$$1.1\times10^{-8} = \frac{[.0750][OH^-]}{[.100M]}$$

$$[OH^-] = 1.47\times10^{-8}\ M$$

$$pOH = -\log[OH^-] = -\log[1.47\times10^{-8}]$$

$$pOH = 7.83$$

$$pH = 14 - 7.83 = \boxed{6.17}$$

2. Buffers

(A) What is a buffer? A solution made from a weak acid and its conjugate base that resists changes to its pH.

(B) Why are buffer solutions resistant to changes in pH when a strong acid or base is added to the solution?

- The weak acid in the buffer neutralizes strong bases & the conjugate base neutralizes strong acids.

(C) What is the Henderson-Hasselbalch equation?

$$pH = pKa + \log \frac{[base]}{[acid]}$$

(D) When choosing a buffer what is a good pH range?

$pH = pKa \pm 1$

(E) A buffer is needed for a solution with a pH of 3.00. Which of the following buffers would be best?

		Ka	pKa
acetic acid	$HC_2H_3O_2 / NaC_2H_3O_2$	1.8×10^{-5}	→ 4.74
ascorbic acid	$H_2C_6H_6O_6 / KC_6H_6O_6$	8.0×10^{-5}	→ 4.10
carbonic acid	$H_2CO_3 / LiHCO_3$	4.3×10^{-7}	→ 6.37
* citric acid	$H_3C_6H_5O_7 / NaH_2C_6H_5O_7$	7.4×10^{-4}	→ 3.13
sulfurous acid	$H_2SO_3 / LiHSO_3$	1.7×10^{-2}	→ 1.77

→ because its pKa is within ±1 of the needed pH.

(F.1) Calculate the pH of a solution that is 1.00M HNO_2 (acid) and 0.900M $NaNO_2$ (base). $Ka = 4.0 \times 10^{-4}$

$$pH = pKa + \log \frac{[base]}{[acid]} = -\log(4.0 \times 10^{-4}) + \log\left(\frac{.900}{1.00}\right)$$

$$pH = 3.40 + -.046 = \boxed{3.35}$$

(F.2) Calculate the pH of the solution in F.1 after .10mol NaOH is added to 1.00L of the solution.

The acid in the buffer reacts with added OH^-

	HNO_2	+ OH^-	→ NO_2^-	+ H_2O
I	1.00M	0	.900M	
C	-.10M	.10M	+.10M	
E	.90M	0	1.0M	

$$pH = pKa + \log \frac{[NO_2^-]}{[HNO_2]}$$ (pKa from F.1)

$$pH = 3.40 + \log\left(\frac{1.0}{.90}\right) = 3.40 + .046$$

$$pH = \boxed{3.45}$$

(F.3) Calculate the pH of the solution in F.1 after adding .30mol of HCl to 1.00L of the solution.

The base in the buffer reacts with added H^+

	← NO_2^-	+ HCl	→ HNO_2	+ Cl^-
I	.900M	0	1.00M	
C	-.30M	.30M	+.30M	
E	.60M	0	1.30M	

$$pH = pKa + \log \frac{[NO_2^-]}{[HNO_2]}$$ (pKa from F.1)

$$pH = 3.40 + \log \frac{[.60]}{[1.30]} = 3.40 + -.34$$

$$pH = \boxed{3.06}$$

(G) How many mols of $NaC_2H_3O_2$ must be added to 1.0 L of 2.0M $HC_2H_3O_2$ to produce a solution buffered to a pH = 5.00.

$K_a = 1.8 \times 10^{-5}$

$pH = pK_a + \log \frac{[base]}{[acid]}$

$5.00 = -\log(1.8 \times 10^{-5}) + \log \frac{[C_2H_3O_2^-]}{[2.0]}$

$5.00 = 4.74 + \log \frac{[C_2H_3O_2^-]}{[2.0]}$

$.260 = \log \frac{[C_2H_3O_2^-]}{[2.0]}$

$10^{.260} = 10^{\log \frac{[C_2H_3O_2^-]}{[2.0]}}$

$10^{.260} = 10$

$.550 = \frac{[C_2H_3O_2^-]}{[2.0]}$

$1.10M = [C_2H_3O_2^-]$

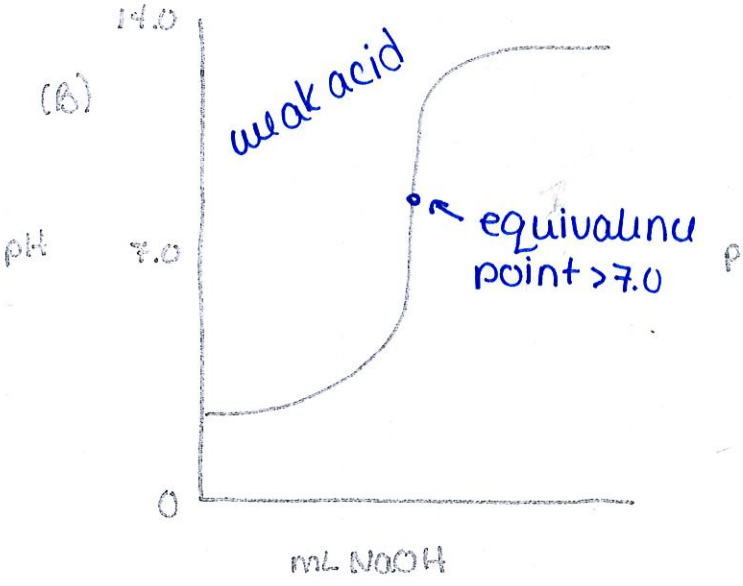
$n = M \cdot V = 1.10M \cdot 1.0L = \boxed{1.10 mol}$

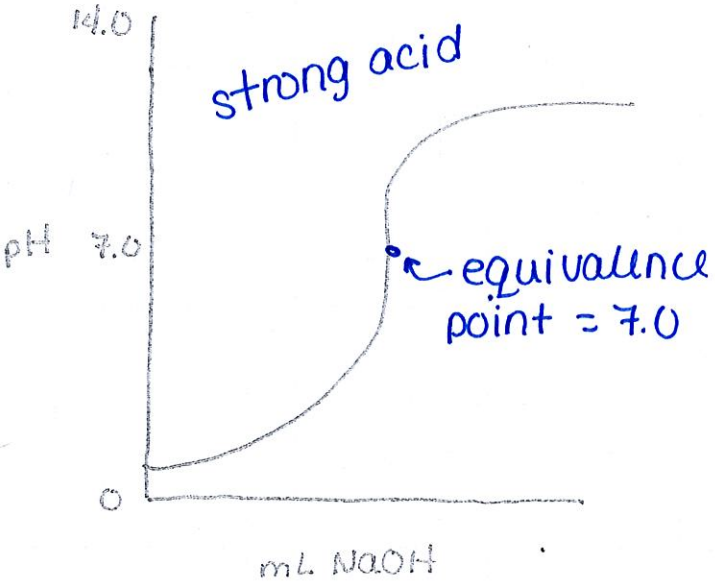
3. Acid - Base Titrations.

(A) what is the equivalence point in a titration?

the point at which the mols of acid = mols of base

(B)





(B.1) Label the titration curve for the strong acid and for the weak acid.

see above.

C. Strong Acid-Strong Base Titration

Consider the titration of 40.0mL of .200M $HClO_4$ by .100M KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.

(C.1) 0.0mL KOH

If no base has been added to the solution, the $[H^+]$ comes directly from $[HClO_4]$.

$pH = -\log(.200) = .699$

(C.2) 10.0mL KOH

All of the OH^- from the KOH neutralizes some of the H^+ from the $HClO_4$. We need to determine how much H^+ remains.

initial → $n_{OH^-} = M \cdot V = .100M \cdot .0100L = 1 \times 10^{-3} mol$

initial → $n_{H^+} = .200M \cdot .0400L = 8 \times 10^{-3} mol$

	H^+	+ OH^-	⇌ H_2O
I	8×10^{-3}	0	
C	-1×10^{-3}	1×10^{-3}	
E	$7 \times 10^{-3} mol$	0	

amount of H^+ from $HClO_4$ remaining.

new V = 40.0mL + 10.0mL = 50.0mL ⇒ .0500L

$[H^+] = \frac{n}{V} = \frac{7 \times 10^{-3} mol}{.0500L} = .14M$

$pH = -\log(.14) = .85$

(C.3) 40.0mL KOH

$n_{OH^-} = .100M \cdot .0400L = 4 \times 10^{-3} mol$

$n_{H^+} = 8 \times 10^{-3} mol$ (same as in C.2)

	H^+	+ OH^-	⇌ H_2O
I	8×10^{-3}	0	
C	-4×10^{-3}	4×10^{-3}	
E	4×10^{-3}	0	

new V = 40.0mL + 40.0mL = 80.0mL ⇒ .0800L

$[H^+] = \frac{4 \times 10^{-3} mol}{.0800L} = .05M$

$pH = -\log .05$

$pH = 1.3$

(C.4) 80.0mL KOH $n_{OH^-} = .100M \cdot .0800L = 8\times10^{-3}$ mol

$n_{H^+} = 8\times10^{-3}$ mol

$n_{H^+} = n_{OH^-}$

All of the H^+ from $HClO_4$ is neutralized by all of the OH^- from KOH, leaving only H_2O.

$\therefore$ pH = 7.0

(C.5) 100.0mL KOH $n_{OH^-} = .100M \cdot .1000L = .010$ mol

$n_{H^+} = 8\times10^{-3}$ mol

	H^+	+ OH^-	$\rightleftharpoons$ H_2O
I	8×10^{-3}	.010mol	
C	-8×10^{-3}	-8×10^{-3}	
E	0	2×10^{-3}	

All of the H^+ is neutralized and we have extra OH^- remaining in solution.

$pOH = -\log(2\times10^{-3}) = 2.70$

pH = 11.30

(D) Consider the titration of 80.0mL of .100M LiOH with .400M HCl. Calculate the pH of the resulting solution after the following volumes of HCl have been added.

(D.1) 0.0mL HCl $pOH = -\log[OH^-] = -\log[.100]$

pOH = 1.0

pH = 14 − 1.0 = **13**

(D.2) 20.0mL HCl

$n_{H^+} = .400M \cdot .020L = .00800$mol

$n_{OH^-} = .100M \cdot .080L = .00800$mol

	OH^-	+ H^+	$\rightleftharpoons$ H_2O
I	.00800mol	0	
C	−.00800mol	.00800mol	
E	0	0	

Since all of the base is neutralized by all of the acid, **pH = 7.0**

(0.3) 30.0 mL HCl

$n_{H^+} = .400M \cdot .0300L = .0120\,mol$

$n_{OH^-} = 8 \times 10^{-3}\,mol$ (from D.2)

	OH^-	+ H^+	⇌ H_2O
I	$8 \times 10^{-3}\,mol$	$.0120\,mol$	
C	$-8 \times 10^{-3}\,mol$	$-8 \times 10^{-3}\,mol$	
E	0	$4 \times 10^{-3}\,mol$	

new V = 80.0mL + 30.0mL
= 110.mL = .110L

$M_{H^+} = \frac{4 \times 10^{-3}\,mol}{.110L} = .0364M$

$pH = -\log[H^+] = -\log[.0364] = \boxed{1.44}$

(0.4) 40.0mL HCl

$n_{H^+} = .400\,M \cdot .040L = .0160\,mol$

$n_{OH^-} = 8 \times 10^{-3}\,mol$

	OH^-	+ H^+	⇌ H_2O
I	8×10^{-3}	.0160	
C	-8×10^{-3}	-8×10^{-3}	
E	0	8×10^{-3}	

new V = 80.0mL + 40.0mL
= 120.mL = .120L

$M_{H^+} = \frac{8 \times 10^{-3}\,mol}{.120L} = .0667\,M$

$pH = -\log[.0667] = \boxed{1.18}$

(0.5) 80.0 mL HCl

$n_{H^+} = .400M \cdot .0800L = .0320\,mol$

$n_{OH^-} = 8 \times 10^{-3}\,mol$

	OH^-	+ H^+	⇌ H_2O
I	8×10^{-3}	.0320	
C	-8×10^{-3}	-8×10^{-3}	
E	0	.0240	

new V = 80.0mL + 80.0mL
= 160.mL = .160L

$M_{H^+} = \frac{.0240\,mol}{.160L} = .15M$

$pH = -\log[.150] = \boxed{.824}$

E. Weak Acid - Strong Base Titrations

Consider the titration of 100.0 mL of .200M $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$) by .100M NaOH. Calculate the pH of the solution after the following volumes of NaOH have been added.

(E.1) 0.0 mL NaOH — Only have to think about the weak acid equilibrium, no base has been added

	$HC_2H_3O_2$	+ H_2O	⇌	$C_2H_3O_2^-$	+	H_3O^+
I	.200M			0		0
C	$-x$			$+x$		$+x$
E	$.200 - x$			x		x

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{.200 - x}$$

✓ assume x will be much smaller than .200.

$$1.8 \times 10^{-5} = \frac{x^2}{.200}$$

$$3.6 \times 10^{-6} = x^2$$

$$1.90 \times 10^{-3} = x$$

$$1.9 \times 10^{-3} M = [H_3O^+]$$

$$-\log(1.9 \times 10^{-3}) = pH$$

$$2.72 = pH$$

(E.2) 50.0 mL NaOH

$n_{OH^-} = .100M \cdot .0500L = 5 \times 10^{-3} mol$

$n_{HC_2H_3O_2} = .200M \cdot .1000L = .02 mol$

So the $HC_2H_3O_2$ is getting neutralized by the OH^-:

	$HC_2H_3O_2$	+ OH^-	→ $C_2H_3O_2^-$	+ H_2O
I	.02 mol	∅	∅	
C	-5×10^{-3} mol	5×10^{-3} mol	$+5 \times 10^{-3}$ mol	
E	.015 mol	∅	5×10^{-3} mol	

(all the OH^- is used up!)

new V = 100.0mL + 50.0mL = 150.0mL

At equilibrium:

$M_{HC_2H_3O_2} = \frac{n}{V} = \frac{.015 mol}{.1500L} = .1 M$

$M_{C_2H_3O_2^-} = \frac{5 \times 10^{-3} mol}{.1500L} = .033 M$

$pH = pKa + \log\left[\frac{base}{acid}\right]$

$pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{.033}{.1}\right)$

$pH = 4.74 + -.48 = 4.26$

(E.3) 200.0 mL NaOH $n_{OH^-} = .100\,M \cdot .2000\,L = .02\,mol$

$n_{HC_2H_3O_2} = .02\,mol$ (from E.2)

	$HC_2H_3O_2$	+ OH^-	→ $C_2H_3O_2^-$	+ H_2O
I	.02 mol	0	0	
C	−.02 mol	.02 mol	+.02 mol	
E	0	0	.02 mol	

All of the acid is neutralized by all of the OH^- BUT there is still $C_2H_3O_2^-$ in the solution! new V = 300.0 mL

$$[C_2H_3O_2^-] = \frac{n}{V} = \frac{.02\,mol}{.300\,L} = .67\,M$$

The $C_2H_3O_2^-$ reacts with H_2O in the solution

	$C_2H_3O_2^-$	+ H_2O	⇌ $HC_2H_3O_2$	+ OH^-
I	.67 M		0	0
C	−x		+x	+x
E	.67 − x		x	x

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_b = 5.6 \times 10^{-10}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{.67 - x} \approx 0$$

$$5.6 \times 10^{-10} = \frac{x^2}{.67}$$

$$3.7 \times 10^{-10} = x^2$$

$$1.93 \times 10^{-5} = x$$

$$1.93 \times 10^{-5} M = [OH^-]$$

$$pOH = -\log(1.93 \times 10^{-5})$$

$$pOH = 4.71$$

$$pH = 9.29$$

(E.4) 250.0mL NaOH $n_{OH^-} = .100M \cdot .2500L = .025mol$

from E.3, we saw we needed .02mol OH^- to neutralize $HC_2H_3O_2$ completely.

∴ if we subtract .025mol − .02mol = .005mol OH^- remains in solution. new V = 350.0L

$$[OH^-] = \frac{n}{V} = \frac{.005mol}{.3500L} = .0143M$$

$$pOH = -\log(.0143M) = 1.85$$

$$pH = 12.15$$

F. Consider the titration of 100.0mL of .100M lactic acid ($HC_3H_5O_3$, $K_a = 1.38 \times 10^{-4}$) by .200M KOH. Calculate the pH of the solution after the following volumes of KOH have been added.

(F.1). 0.0mL KOH

$$HC_3H_5O_3 + H_2O \rightleftharpoons C_3H_5O_3^- + H_3O^+$$

	$HC_3H_5O_3$	H_2O	$C_3H_5O_3^-$	H_3O^+
I	.100M		0	0
C	−x		+x	+x
E	.100 − x		x	x

$$K_a = \frac{[C_3H_5O_3^-][H_3O^+]}{[HC_3H_5O_3]}$$

$$1.38 \times 10^{-4} = \frac{(x)(x)}{(.100 - \cancel{x}^{0})}$$

$$1.38 \times 10^{-4} = \frac{x^2}{.100}$$

$$1.38 \times 10^{-5} = x^2$$

$$3.71 \times 10^{-3} = x$$

$$3.71 \times 10^{-3} M = [H_3O^+]$$

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

$$pH = -\log[3.71 \times 10^{-3}]$$

$$\boxed{pH = 2.43}$$

(F.2) 25.0 mL KOH

$n_{OH^-} = .200M \cdot .0250L = 5 \times 10^{-3}$ mol

$n_{HC_3H_5O_3} = .100M \cdot .1000L = .01$ mol

	$HC_3H_5O_3$	+ OH^-	⇌ $C_3H_5O_3^-$	+ H_2O
I	.01 mol	∅	∅	
C	-5×10^{-3} mol	5×10^{-3} mol	$+5\times10^{-3}$ mol	
E	5×10^{-3} mol	∅	5×10^{-3} mol	

new V = 100.0 mL + 25.0 mL = 125.0 mL = .1250 L

$[HC_3H_5O_3] = [C_3H_5O_3^-] = \frac{5\times10^{-3}\text{ mol}}{.1250L} = .0400M$

$pH = pKa + \log\frac{[C_3H_5O_3^-]}{[HC_3H_5O_3]} = -\log(1.38\times10^{-4}) + \log\left(\frac{.0400}{.0400}\right) = 3.86 + 0$

$pH = \boxed{3.86}$

(F.3) 50.0 mL KOH

$n_{OH^-} = .200M \cdot .0500L = .01$ mol

$n_{HC_3H_5O_3} = .01$ mol (from F.2)

new V = 100.0 mL + 50.0 mL = 150.0 mL = .1500 L

	$HC_3H_5O_3$	+ OH^-	⇌ $C_3H_5O_3^-$	+ H_2O
I	.01 mol	∅	∅	
C	−.01 mol	.01 mol	+.01 mol	
E	∅	∅	.01 mol	

$[C_3H_5O_3^-] = \frac{.01\text{ mol}}{.1500L} = .0667M$

reacts w/ H_2O

	$C_3H_5O_3^-$	+ H_2O	⇌ $HC_3H_5O_3$	+ OH^-
I	.0667M		∅	∅
C	−x		+x	+x
E	.0667 − x		x	x

$K_b = \frac{[HC_3H_5O_3][OH^-]}{[C_3H_5O_3^-]}$

$K_b = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.38\times10^{-4}}$

$K_b = 7.25\times10^{-11}$

$7.25\times10^{-11} = \frac{(x)(x)}{(.0667-x)} \approx$

$7.25\times10^{-11} = \frac{x^2}{.0667}$

$4.83\times10^{-12} = x^2$

$2.20\times10^{-6} = x$

$[OH^-] = 2.20\times10^{-6}M$

$pOH = -\log(2.20\times10^{-6}) = 5.66$

$pH = 14 - 5.66 = \boxed{8.34}$

(F.4) 100.0mL KOH

$n_{OH^-} = .200 \cdot .1000L = .0200M$

$n_{HC_3H_5O_3} = .0100\,mol$

new V = 100.0mL + 100.0 mL
= 200.0mL = .2000L

$HC_3H_5O_3 + OH^- \rightleftharpoons C_3H_5O_3^- + H_2O$

I	.0100 mol	.0200 mol	0	/
C	-.0100	-.0100	+.0100	
E	0	.0100	.0100	

$[OH^-] = \frac{.0100 mol}{.2000L} = .0500M$

$pOH = -\log(.0500) = 1.30$

$pH = 14 - 1.30 = \boxed{12.7}$

4. Solubility Equilibria

(A) which of the following substances is least soluble? most soluble?

	K_{sp}
MgF_2	6.4×10^{-9}
$PbBr_2$	4.6×10^{-6}
$AgBr$	5.0×10^{-13}
Ag_2SO_4	1.2×10^{-5}
$CaSO_4$	6.1×10^{-5}

The least soluble substance has the smallest K_{sp},

∴ AgBr is least soluble

$CaSO_4$ is most soluble

(B) what is the effect on equilibrium when a common ion is added to a solution of $PbSO_4$?

The solubility of $PbSO_4$ decreases as equilibrium is shifted to the left.

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

(C) The Ksp for $PbBr_2$ is 4.6×10^{-6}. Calculate the solubility, in g/L, of $PbBr_2$ in a solution that contains .040M NaBr.

$PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^-$

		Pb^{2+}	Br^-
I		0	.040M
C		+x	+2x
E		x	.040 + 2x

$4.6 \times 10^{-6} = (x)(.040 + 2\cancel{x}^{0})^2$

$4.6 \times 10^{-6} = .040\,x$

$1.15 \times 10^{-4} = x$

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

$[PbBr_2] = 1.15 \times 10^{-4}\,M$

$1.15 \times 10^{-4} \frac{mol}{L}\left(\frac{367.9}{1\,mol}\right) = \boxed{.0422 \frac{g}{L}}$

(D) A saturated solution of $Cd(OH)_2$ in contact with undissolved solid at 25°C has a pH of 9.36. Assuming $Cd(OH)_2$ completely ionizes, calculate Ksp.

$pOH = 14 - 9.36 = 4.64$

$[OH^-] = 10^{-4.64} = 2.29 \times 10^{-5}\,M$

$Cd(OH)_2 \rightleftharpoons Cd^{+2} + 2OH^-$

$1.15 \times 10^{-5}\,M$ ($\frac{1}{2}$ of $[OH^-]$) $\quad 2.29 \times 10^{-5}\,M$

$K_{sp} = [Cd^{2+}][OH^-]^2 = [1.15 \times 10^{-5}][2.29 \times 10^{-5}]^2$

$K_{sp} = \boxed{6.03 \times 10^{-15}}$