## VERSION 1.

Enter your version number in the correct column on your scan sheet (see p. 2 for details).

- 1. Which of the following is a **strong acid**?
  - A) **HBr**
  - B) H<sub>3</sub>PO<sub>4</sub>
  - C) HOCl
  - D) H<sub>2</sub>O
  - E) HClO<sub>2</sub>

Strong acids are HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>

- 2. A student prepares a 0.1 M aqueous solution of 2,4-dinitrophenol ( $pK_a = 4.11$ ) to serve as pH indicator. What is the **pH** of this indicator solution, and what is the **pH range** best probed by this indicator, respectively?
  - A) 3.8; 6.2 8.2
  - B) 2.6; 4.2 6.2
  - C) 3.8; 3.1 5.1
- 2,4-dinitrophenol has a low p $K_a$  (4.11) therefore it is a weak acid

$$\mathrm{HA} + \mathrm{H}_2\mathrm{O} \, \rightarrow \, \mathrm{H}_3\mathrm{O}^+ + \mathrm{A}^-$$

C) 3.8; 3.1 – 5.1  
D) 5.2; 6.2 – 8.2  
E) 2.6; 3.1 – 5.1  

$$C$$
 –  $C$  –  $C$ 

 $\frac{0.1}{7.7_{625} \times 10^{-5}} = 1288 > 100; \text{ therefore small x approximation is valid}$ 

$$7.7_{625} \times 10^{-5} = \frac{x^2}{0.1}$$
;  $x = 2.786 \times 10^{-5} = [H_3O^+]$ 

$$pH = -log[H_3O^+] = -log(2.786 \times 10^{-5}) = 2.555 \approx 2.6$$

The pH range best probed by an indicator is between a ratio of 0.1 to 10 of its conjugate acid and base concentrations and corresponds to a pH range of its pKa ± 1. Therefore 3.1 - 5.1.

- 3. A buffer is prepared by adding 0.5 mol of solid sodium hydroxide to 1.0 L of 1.0 M weak acid (HA). What is the **pH** of the buffer?
  - A) The pH will be  $pK_a 0.30$ , where  $pK_a$  is that of the weak acid.
  - B) The pH will be equal to the  $pK_a$  for the weak acid.
  - C) The pH will be greater than the  $pK_a$  for the weak acid.
  - D) The pH will be less than the p $K_a$  for the weak acid but greater than p $K_a 0.30$ .
  - E) The pH will be less than the value in answer (A).

Before 
$$HA + NaOH \rightarrow H_2O + NaA$$
 (note: this fully dissociates and =  $Na^+ + A^-$ )  
After  $0.5 \quad 0 \quad 0.5 \quad 0.5$ 

Number of moles of  $A^-$  = number of moles of HA

$$pH = pK_a + \log (A^-/HA) = pK_a + \log (0.5/0.5) = pK_a$$

4. What is the **pH** of a 0.015 M solution of ethylamine (CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>, aq)?

Data:  $K_b = 4.3 \times 10^{-4}$  CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> is a weak base  $K_b = 4.3 \times 10^{-4}$ 

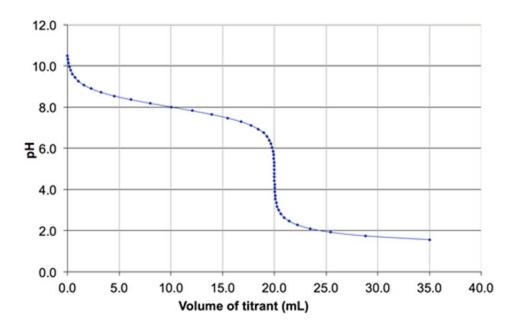
- A) 11.39 I = 0.015 0 = 0
- B) 11.32 C) 11.35 C -x +x +x
- E 0.015-x + x + y
- D) 11.42
- E)  $\frac{0.015}{4.3 \times 10^{-4}}$  = 35 < 100; therefore small x approximation is **NOT** valid

$$4.3 \times 10^{-4} = \frac{x^2}{0.015 - x}$$
;  $6.45 \times 10^{-6} - 4.3 \times 10^{-4} \text{ x} - \text{x}^2 = 0$ ;

using quadratic 
$$x = 2.3_{34} \times 10^{-3} = [OH^{-}]$$
  
pOH =  $-log[OH^{-}] = -log (2.3_{34} \times 10^{-3}) = 2.63_{190} \approx 2.63$ 

$$pH = 14.00 - pOH = 14.00 - 2.63 = 11.37$$

5. Indicate the **FALSE** statement with regard to the titration graph below:



- A) A weak acid is present at the equivalence point.
- B) Phenol Red  $(K_a = 3.2 \times 10^{-8})$  would not be a suitable pH indicator for this titration.
- C) The graph shows the titration of a weak base (beaker) with a strong acid (buret).
- D) The graph shows the titration of a strong base (beaker) with a weak acid (buret).
- E) The graph shows a buffer region centered around pH 8.

If D were true, the equivalence point would be basic and the buffer region would occur after the equivalence point.

- 6. Which of the following combinations of aqueous solutions will produce a **buffer solution**? (All solutions are 1.0 M).
  - A) 50 mL HBr + 25 mL NaOH
  - B)  $50 \text{ mL HBrO}_2 + 20 \text{ mL NaOH}$
  - C) 50 mL HBr + 50 mL NaBr
  - D)  $50 \text{ mL HBrO}_2 + 50 \text{ mL NaOH}$
  - E) 50 mL NaBrO<sub>2</sub> + 50 mL HCl

strong acid and strong base ≠ buffer this would give a 2:3 ratio of BrO<sub>2</sub><sup>-</sup>: HBrO<sub>2</sub> strong acid and its conjugate base ≠ buffer this would convert entirely to weak base form this would convert entirely to weak acid form

D and E are like the equivalence point of a titration, which is beyond the buffer region.

7. (i) Which of the weak acids listed below would be the best choice to prepare a buffer with a pH of 3.0, and (ii) which reagent (HCl or NaOH) should be added to that weak acid to produce the buffer? buffer range possible

			bullet range possible
HClO <sub>2</sub> ,	$K_a = 1.1 \times 10^{-2}$	$pK_a = 1.95_{86}$	0.96 - 2.96
HNO <sub>2</sub> ,	$K_a = 7.2 \times 10^{-4}$	$pK_a = 3.14_{27}$	2.14 - 4.14
-/	$K_a = 1.8 \times 10^{-5}$	$pK_a = 4.74_{47}$	3.74 - 5.74

A)	Weak acid (i) CH <sub>3</sub> COOH,	Reagent (ii) HCl	Therefore a buffer based on HNO <sub>2</sub> can be adjusted to reach pH 3.0.
B)	(i) HNO <sub>2</sub> ,	(ii) HCl	
$\mathbf{C}$	(i) HNO <sub>2</sub> ,	(ii) NaOH	HNO <sub>2</sub> is a weak acid and requires addition of a
D)	(i) HClO <sub>2</sub>	(ii) HCl	limiting amount of strong base to produce a buffer

(ii) HCl

(ii) NaOH

8. Which of the following indicators is best suited to determine the equivalence point of a titration of acetic acid with a strong base?

in the appropriate pH range.

Data:  $pK_a$  (acetic acid) = 4.74

D) (i) HClO<sub>2</sub>,

(i) HClO<sub>2</sub>,

E)

- Alizarin Yellow-R (p $K_{HIN} \approx 11$ ) A)
- Phenolphthalein (p $K_{HIN} \approx 9$ )  $\mathbf{B}$
- Bromothymol Blue (p $K_{HIN} \approx 6.5$ ) C)
- Methyl Violet (p $K_{HIN} \approx 1$ ) D)
- Bromcresol Blue (p $K_{HIN} \approx 4$ ) E)

At the equivalence point acetic acid (HA) is entirely converted to its weak base form (A<sup>-</sup>) with a p $K_b = 9.26$ .

Therefore an indicator that changes colour in the weakly basic range is best suited to determine the equivalence point. With a  $pK_{HIN} \approx 9$ , Phenolphthalein would change over a range of 8 to 10 and would be ideal.

- 9. Which of the following bases has the strongest conjugate acid?
  - A)  $C_6H_5O^-$  (phenoxide),  $K_b = 9.1 \times 10^{-9}$

  - B)  $C_6H_5NH_2$  (aniline),  $K_b = 7.4 \times 10^{-10}$ C)  $C_6H_5COO^-$  (benzoate),  $K_b = 1.6 \times 10^{-10}$
  - D)  $CN^{-}$  (cyanide),  $K_b = 1.6 \times 10^{-5}$
  - E) HONH<sub>2</sub> (hydroxylamine),  $K_b = 9.1 \times 10^{-9}$

Weakest base (smallest  $K_b$ ) has the strongest conjugate acid (largest  $K_a$ ).

- 10. A student is titrating 100.0 mL of 0.25 M HNO<sub>2</sub> (beaker;  $K_a = 7.2 \times 10^{-4}$ ) with 0.10 M KOH (buret). Determine the **FALSE** statement regarding the titration curve that would be produced.
  - A) There is a maximum buffer capacity of the titration solution at pH = 3.14.
  - The pH at the equivalence point will be basic.
  - C)  $pK_b(NO_2^-) = pOH$  at the half-equivalence point of the titration.
  - The curve would begin at a pH greater than 1.
  - The titration would reach an equivalence point at a volume less than 100.0 mL of KOH added.

At the equivalence point moles of strong base equals moles of weak acid. From this, the volume of KOH needed to reach the equivalence point can be determined.

5

 $C_1V_1 = C_2V_2$ ;  $(0.25 \text{ M})(0.1000 \text{ L}) = (0.10 \text{ M})(V_{KOH})$ ;  $V_{KOH} = 0.25 \text{ L} = 250 \text{ mL}$ 

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11. Ideal blood pH is 7.4. A patient suffering from acidosis is found to have pH = 7.0. Based on the reaction below, what is the **ratio of [HCO<sub>3</sub>-]** / [ $H_2CO_3$ ] in this patient's blood?

$$H_2CO_3(aq) + H_2O(1) \longrightarrow HCO_3^-(aq) + H_3O^+(aq)$$

Data: 
$$K_a$$
 (H<sub>2</sub>CO<sub>3</sub>) = 4.5 × 10<sup>-7</sup>   
p $K_a$  =  $-\log K_a$  = 6.347   
pH =  $pK_a$  +  $\log ([HCO_3^-] / [H_2CO_3])$    
7.0 = 6.347 +  $\log ([HCO_3^-] / [H_2CO_3])$    
0.653 =  $\log ([HCO_3^-] / [H_2CO_3])$    
C) 0.24   
D) 0.44   
10<sup>0.653</sup> =  $[HCO_3^-] / [H_2CO_3]$    
[HCO<sub>3</sub><sup>-</sup>] / [H<sub>2</sub>CO<sub>3</sub>] = 4.5

- 12. A buffer solution consists of the carbonate ion (CO<sub>3</sub><sup>2-</sup>) and hydrogen carbonate ion (HCO<sub>3</sub><sup>-</sup>) conjugate acid-base pair. Which of the following such buffers (all 1 L) can neutralize the greatest amount of added hydrochloric acid, while remaining within its buffer range?
  - A) 0.1 M CO<sub>3</sub><sup>2-</sup> and 0.9 M HCO<sub>3</sub><sup>-</sup>

E) 0.68

- B) 0.1 M CO<sub>3</sub><sup>2-</sup> and 0.1 M HCO<sub>3</sub><sup>-</sup> C) 0.9 M CO<sub>3</sub><sup>2-</sup> and 0.1 M HCO<sub>3</sub><sup>-</sup> D) 0.9 M CO<sub>3</sub><sup>2-</sup> and 0.9 M HCO<sub>3</sub><sup>-</sup>

- E)  $0.5 \text{ M CO}_3^{2-}$  and  $0.5 \text{ M HCO}_3^{-}$

In order to neutralize the **greatest amount of acid**, you want the largest ratio of conjugate base:conjugate acid. While D and E form "ideal buffers" (they have the best ratio to react with added strong acid OR strong base) they would not be able to neutralize as much HCl while staying within their buffer regions.

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- 13. In the titration of a weak base with a strong acid, the solution at the **equivalence point** is?
  - A) strongly basic
  - B) weakly basic
  - C) strongly acidic
  - D) weakly acidic
  - E) neutral

e.g. 
$$A^- + HCl \rightarrow HA + Cl^-$$

weak base is entirely converted to conjugate weak acid

14. A solution of pH 3.88 is prepared by dissolving sufficient sodium formate, NaHCOO(s), in 1.50 L of 0.100 M formic acid (HCOOH). How many **mol of NaOH(s)** must be added to change the pH by 0.40 units? Assume no volume changes on addition of solids.

```
Data: K_a (HCOOH) = 1.8 \times 10^{-4}
                                       First we must determine the amount of HCOO present
                                       in solution.
A) 0.025
                                       n_{HCOOH} = C_{HCOOH}V_{HCOOH} = 0.100 \text{ M} \text{ x } 1.50 \text{ L}
                                                = 0.150 \text{ mol}
B) 0.010
                                       pK_a = -\log K_a = 3.7447
     0.070
C)
                                       pH = pK_a + log ([HCOO^-] / [HCOOH])
D) 0.040
                                       and since C = n/V and the V is the same in the same
E)
    0.10
                                       vessel,
                                       pH = pK_a + log (n_{HCOO-} / n_{HCOOH})
                                       3.88 = 3.7447 + \log \left( \frac{n_{HCOO}}{0.150} \right)
                                       n_{HCOO-} = 0.205
```

The strong base will react with the weak acid of the buffer. Since the change in pH is small, and the solution remains within the buffer range, the amount of NaOH must be limiting.

```
\begin{array}{cccc} & HCOOH + NaOH \rightarrow H_2O + NaHCOO \\ Before & 0.150 & x & 0 & 0.205 \\ After & 0.150 - x & 0 & x & 0.205 + x \end{array}
```

With addition of base, pH increases. Therefore a change in pH of 0.40 from 3.88 is 4.28.

```
pH = pK_a + log (n_{HCOO-} / n_{HCOOH})
4.28 = 3.7447 + log [(0.205 - x)] / (0.150 - x)]
x = 0.070
```

15. What is the **pH** of the solution that results when the following substances are added to water to create 1.00 L of solution?

Data: 
$$K_a$$
 (HClO<sub>2</sub>) = 1.1 × 10<sup>-2</sup>

Before 0.150 0.100 0 0.0800

0.100 mol NaOH

0.150 mol HClO<sub>2</sub>

0.0800 mol NaClO<sub>2</sub>

Since all in 1L water, # moles = concentration

 $pK_a = -\log K_a = 1.95_{86}$ 

A) 1.74

PM =  $pK_a + \log (|N_BClO_A|/|HClO_A|)$ 

B) 2.21  
C) 1.96  
D) 2.51  
E) 1.88  

$$pH = pK_a + log ([NaClO_2] / [HClO_2])$$

$$= 1.95_{86} + log (0.1800 / 0.050)$$

$$= 2.51$$

16. **How many mL** of 0.10 M NaOH do you need to add to 100. mL of 0.10 M HCl to get a solution with a pH of 3.00?

- 17. Indicate the **pH** at the equivalence point of a titration of a 0.050 M aqueous solution of trimethylamine ( $K_b = 6.3 \times 10^{-5}$ ) with 0.10 M HCl.
  - A) 4.92
  - B) 5.64
  - C) 3.90
  - D) 5.12
  - E) 4.33

Titration of 0.050 M weak base with 0.10 M HCl will give the same pH at the equivalence point regardless of the volume that was initially used. To make the calculation easier, assume that 1.00 L of 0.050 M was titrated (this may be unrealistic but makes the calculation easier).

Therefore 0.050 mol of trimethylamine [B] was titrated

to equivalence requiring 0.050 mol of HCl.  $V_{HCl} = n_{HCl}/C_{HCl} = 0.050/0.10 = 0.50 L$  $V_{\text{Tot}} = V_{\text{trimethylamine}} + V_{\text{HCI}} = 1.00 \text{ L} + 0.50 \text{ L} = 1.50 \text{ L}$ 

 $[BH^{+}]$  at equivalence point = 0.050 mol/1.50L

$$BH^{+} + H_{2}O \rightarrow H_{3}O^{+} + B$$

$$I \qquad 0.033_{33} \qquad 0 \qquad 0$$

$$C \qquad -x \qquad +x \qquad +x$$

$$E \qquad 0.033_{33} - x \qquad +x \qquad +x$$

$$K_{a} = K_{w}/K_{b} = 1.0 \times 10^{-14}/6.3 \times 10^{-5} = 1.5_{873} \times 10^{-10}$$

$$K_a = K_w/K_b = 1.0 \times 10^{-14}/6.3 \times 10^{-5} = 1.5_{873} \times 10^{-10}$$

 $\frac{0.033_{33}}{1.5_{873} \times 10^{-10}}$  = 2.1 × 10<sup>8</sup> > 100; therefore small x approximation is valid

$$1.5_{873} \times 10^{-10} = \frac{x^2}{0.033_{33}}; \quad x = 2.3_{00} \times 10^{-6} = [H_3O^+]$$
  
 $pH = -log[H_3O^+] = -log(2.3_{00} \times 10^{-6}) = 5.64$ 

- 18. Which of the following statements about buffers is **FALSE**?
  - A) A buffer with weak acid HA, with a given  $K_a$ , operates most effectively over a pH range of p $K_a \pm 1$ .
  - B) Weak acid-strong base titration curves show a buffer region centered around the half-equivalence point.
  - The percent ionization of the weak acid in a buffer is much less than the percent ionization of a weak acid alone.
  - A buffer can be produced by reacting a strong acid with a limiting amount of weak D) base.
  - A buffer can be destroyed by adding a large excess of water.

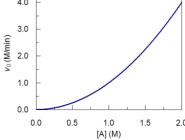
If the weak base is limiting, then strong acid remains and solely determines pH. The correct statement should read: A buffer can be produced by reacting a weak base with a limiting amount of strong acid.

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- 19. Which of the following statements is **FALSE** regarding the rate law,  $v_0 = k[A]^2[B][C]$ ?
  - A) The slope of the graph of  $v_0$  vs [A] is positive.
  - B) Altering [B] by a given factor vs altering [C] by the same factor will result in the same change in  $v_0$ .
  - C) The graph of  $v_0$  vs [A] is linear.
  - D) The rate constant, k, is the rate when the concentrations of A, B, C are all 1 M.
  - E) Changing [C] and [A] each by a factor of 3 results in a 27-fold increase in  $v_0$ .

The graph would be curved and would resemble the graph that appears on slide 24 in the course notes.



20. Based on the observed rates in the four experiments below, what is the **rate law** for the reaction  $3A + 2B + C \rightarrow G$ ?

[A](M)	[B](M)	[C](M)	$v_0 (M/s)$
0.600	0.300	0.300	0.200
0.300	0.600	0.600	0.050
0.300	0.300	0.600	0.100
0.900	0.300	0.300	0.450

- A)  $v_0 = k[A]^2[B][C]$
- B)  $v_0 = k[A]^2[B]^{-1}[C]$
- C)  $v_0 = k[A][B]^{-1}[C]$
- D)  $v_0 = k[A][B]^2[C]$
- E)  $v_0 = k[A]^2[B][C]^{-1}$

$$v_0 = k[A]^m[B]^n[C]^y$$

For reactant A, use trial 1 and 4

$$v_0(4)/v_0(1) = 2.25$$

$$= k(0.900)^{\mathrm{m}}(0.300)^{\mathrm{n}}(0.300)^{\mathrm{y}}/(0.600\mathrm{M})^{\mathrm{m}}(0.300)^{\mathrm{n}}(0.300)^{\mathrm{y}}$$

$$=(1.5)^{m} \rightarrow m = 2$$

For reactant C, use trial 1 and 3, and m = 2 from previous step.  $v_0(3)/v_0(1) = 0.5$ 

$$= k(0.300)^{2}(0.300)^{n}(0.600)^{y}/(0.600M)^{2}(0.300)^{n}(0.300)^{y}$$
  
=  $(0.5)^{2}(2)^{y} = (0.25)(2)^{y} \rightarrow y = 1$ 

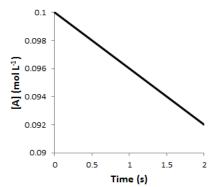
For reactant B, use trial 2 and 3, and m = 2 and y = 1 from previous steps.

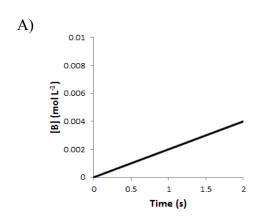
$$v_0(2)/v_0(3) = 0.5$$

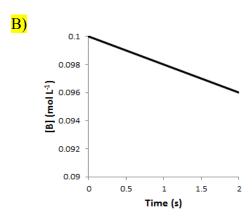
$$= k(0.300)^{2}(0.600)^{n}(0.600)^{y}/k(0.300)^{2}(0.300)^{n}(0.600)^{y}$$

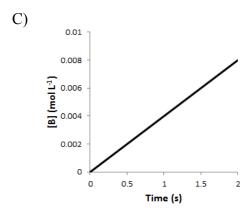
$$= (2)^n \rightarrow n = -1$$

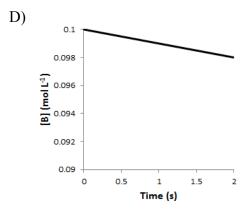
21. For the reaction  $2A + B \rightarrow 2C + 3D$ , the graph of [A] vs t is given below. Which graph best represents [B] vs t?

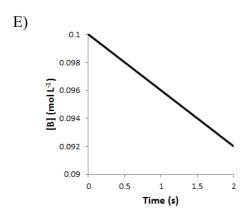












Average rate = 
$$-\frac{1}{2} \underline{\Delta}[A] = -\underline{\Delta}[B]$$
  
 $\underline{\Delta}[A] = -\underline{\Delta}[B]$   
 $\underline{\Delta}[A] = -\underline{\Delta}[B]$ 

Therefore  $\Delta[B]$  over the 2s timeframe is -0.004

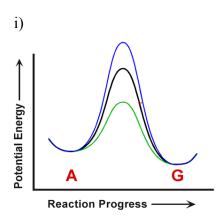
- 22. Which of the following reaction rates would **NOT** be increased by increasing the concentration of B?
  - i)  $v_0 = k[A]^2[B]^{-1}[C]$
  - ii)  $v_0 = k[A]^2[B][C]^{-1}$
  - iii)  $v_0 = k[A]^2[B][C]$
  - iv)  $v_0 = k[A][B]^0[C]$
  - v)  $v_0 = k[A][B]^2[C]$
  - A) iv, v
  - B) iii, v
  - C) i, iv
  - D) i, ii
  - E) ii, iii

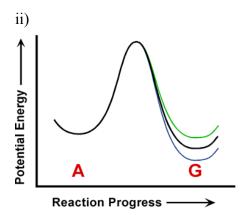
- i) With an exponent of -1 this would result in a decrease in rate with increasing [B].
- iv) With an exponent of 0 this would result in no effect on the rate with increasing [B].

- 23. Which of the following statements is **FALSE** regarding the rate of a chemical reaction?
  - A) Rate is change in concentration over time.
  - B) Rates can change during a reaction.
  - C) Rates are always positive.
  - When relating rates of product appearance and reactant consumption for a given reaction, stoichiometry does not matter.
  - E) The average rate and instantaneous rate in some cases are the same.

When relating rates of product appearance and reactant consumption for a given reaction, stoichiometry **DOES** matter. See slide 9 from the Ch 14 notes.

24. Which statement **best describes** what each the following graphs indicates for the reaction  $A \rightarrow G$ ?





- A) i) degrees of spontaneity and ii) different yields at equilibrium
- B) i) different yields at equilibrium and ii) degrees of spontaneity
- i) different equilibrium positions and ii) degrees of spontaneity
- i) different rates of reaction and ii) different equilibrium positions
- i) different equilibrium positions and ii) different rates of reaction

See slides 2 and 3 from the Ch 14 notes.

25. The rate law for the reaction A + B  $\rightarrow$  3C was determined to be  $v = k[A]^2[B]^2$  at 20°C. If the reaction rate is  $4.0 \times 10^{-5}$  Ms<sup>-1</sup> when [A] = 0.1 M and [B] = 0.2 M, what is the rate constant, k?

A) 
$$4.6 \times 10^{-2} \,\mathrm{M}^{-2} \mathrm{s}^{-1}$$

$$v = k[\mathbf{A}]^2 [\mathbf{B}]^2$$

B) 
$$1.0 \times 10^{-1} \,\mathrm{M}^{-3} \mathrm{s}^{-1}$$

A) 
$$4.6 \times 10^{-2} \,\mathrm{M}^{-2} \mathrm{s}^{-1}$$
  
B)  $1.0 \times 10^{-1} \,\mathrm{M}^{-3} \mathrm{s}^{-1}$   
C)  $8.7 \times 10^{-1} \,\mathrm{M}^{-3} \mathrm{s}^{-1}$   
D)  $8.7 \times 10^{-1} \,\mathrm{M}^{-2} \mathrm{s}^{-1}$   
E)  $4.6 \times 10^{-2} \,\mathrm{M}^{-3} \mathrm{s}^{-1}$   
 $v = k[A]^2[B]^2$   
 $4.0 \times 10^{-5} \,\mathrm{M} \mathrm{s}^{-1} = k = 1.0 \times 10^{-5} \,\mathrm{M} \mathrm{s}^{-1} = 1.0 \times 10^{-5} \,\mathrm{M} \mathrm{s}$ 

D) 
$$8.7 \times 10^{-1} \,\mathrm{M}^{-2} \mathrm{s}^{-1}$$

$$4.0 \times 10^{-5} \,\mathrm{Ms}^{-1} = k[0.1\mathrm{M}]^2 [0.2\mathrm{M}]^2$$
$$k = 1.0 \times 10^{-1} \,\mathrm{M}^{-3} \mathrm{s}^{-1}$$