Name_____ **KEY** 0/19/11

Read questions carefully to understand what is being asked. If you have doubt, ask your instructor. Use the reverse side of your answer paper as scratch. Use attached periodic table and important constants chart. (Total pts. = 50 + 3x11 (33) = 83)

SHORT ANSWER: Show all your calcualtions using appropriate set up and units.

1) Activation energies of reactions, E_a, are frequently found graphically. The Arrhenius   1) _____
equation: $\ln (k) = ((- E_a))/RT + \ln(A)$ is used. Values of k, the rate constant, are measured at various temperatures, then ln k and 1/T are calculated and plotted.
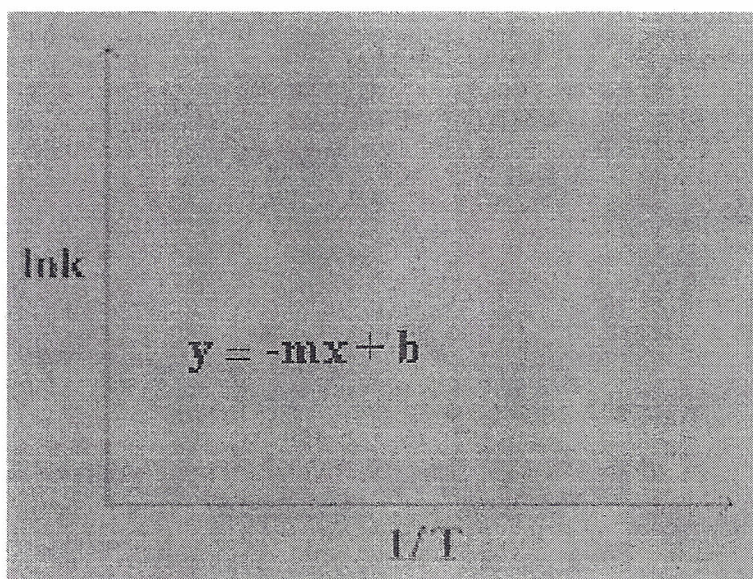
In one particular experiment the, co-ordinates of two points: one at upper left is A(.0013,-3.8) and the other at lower right is B(0.0017, -12.8). Using this information:

(a) Calculate the slope of the st. line (4 pts.)

$(.0013, -3.8) (.0017, -12.8)$

$slope = \dfrac{\Delta y}{\Delta x} = \dfrac{-3.8 - ^-12.8}{.0013 - .0017} = \dfrac{9}{-4\times10^{-4}} = -22500$

$\boxed{slope = ^-22500}$

(b) Calculate the energy of activation of the reaction (Ea) in kilo Joules (6 pts.)

$slope = \dfrac{-E_a}{R}$ $R = 8.3145 \, J/mol \cdot K$

$E_a = ^-slope \, (R)$

$E_a = ^-22500 \, K \left| \dfrac{8.3145 \, J}{mol \cdot K} \right| \dfrac{1 KJ}{1000 J}$ $187.1 \, kJ/mol$

$\boxed{E_a = 187.1 \, kJ/mol \text{ of rxn}}$

1

2) 2.0 g Salicylic Acid ($C_7H_6O_3$) was heated with 5.0 mL acetic anhydride ($C_4H_6O_3$; 2) _____
   density=1.08 g/mL) to get 2.15 g of Aspirin ($C_9H_8O_4$).
   (a) Calculate the limiting reagent (4 pts.)

salicylic acid + acetic anhydride → asprin + acetic acid

$$C_7H_6O_3 + C_4H_6O_3 → C_9H_8O_4 + CH_3CO_2H$$
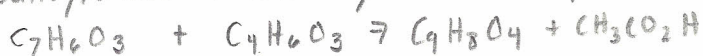
$$2g \; salicylic \; acid \left| \frac{1mol \; C_7H_6O_3}{138.2g} \right. = .0145 mol \; salicylic \; acid$$

$$5ml \; acetic \; anhydride \left| \frac{1.08g}{mL} \right| \frac{1mol \; C_4H_6O_3}{102.1g} = .0529 \; mol \; acetic \; anhydride.$$
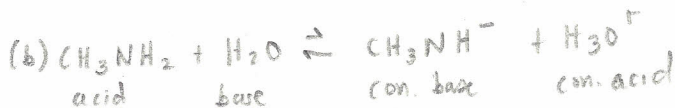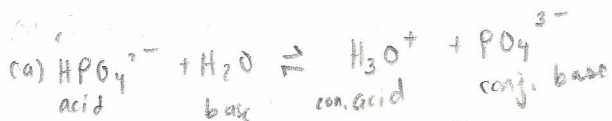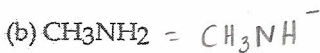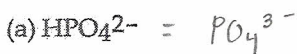
Salicylic acid is the limiting reagent.

Since the mole ratio is 1 to 1, the .0145 mol of salicylic acid is much less than the .0529 mol of acetic anhydride. Hence, salicylic acid is the limiting reagent.

   (b) Calculate the theoretical yield of aspirin (4 pts.)

$$.0145 mol \; salicylic \; acid \left| \frac{1 mole \; asprin}{1 mol \; salicylic \; acid} \right| \frac{180.17g}{1 mole \; asprin} = 2.61g$$

Theoretical Yield : 2.61g of Asprin

   (b) Calculate the percentage yield of aspirin (2 pts.)

$$\% \; Yield = \frac{Actual \; Yield}{Theoretical \; Yield} \times 100 → \frac{2.15g}{2.61g} \times 100 =$$

% Yield : 82.4 %

3) Write the formula of the conjugate base next to the following species (2 pts/each, 6   3) _____
   pts total):

   (a) $HPO_4{}^{2-}$ = $PO_4{}^{3-}$

   (b) CH_3NH_2 = CH_3NH^-

   (c) OH^- = O^{2-}

(a) $\underset{acid}{HPO_4{}^{2-}} + \underset{base}{H_2O} \rightleftharpoons \underset{con. \; acid}{H_3O^+} + \underset{conj. \; base}{PO_4{}^{3-}}$

(b) $\underset{acid}{CH_3NH_2} + \underset{base}{H_2O} \rightleftharpoons \underset{con. \; base}{CH_3NH^-} + \underset{con. \; acid}{H_3O^+}$

(c) $\underset{acid}{OH^-} + \underset{base}{H_2O} \rightleftharpoons \underset{conj. \; base}{O^{2-}} + \underset{conj. \; acid}{H_3O^+}$

$C = 12.01$
$H = 1.01$
$O = 16$

4) The initial rate of the reaction A + B -----> C was measured at several different concentrations of the reactants. Following **formal** methods, (a) calculate the rate law for the reaction (6 pts.) and (b) The magnitude of the rate constant (4 pts.).

4) _____

Experiment	Initial Concentrations [A] (M)	[B] (M)	Initial Rate (M s^{-1})
1	0.010	0.10	4.0 x 10^{-5}
2	0.010	0.20	4.0 x 10^{-5}
3	0.020	0.10	16.0 x 10^{-5}

(a) $Rate = K[A]^m[B]^n$

$\dfrac{Exp\ 2}{Exp\ 1} = \dfrac{K(.01)^m(.2)^n}{K(.01M)^m(.1M)^n} = \dfrac{(.2)^n}{(.1)^n} = \left(\dfrac{.2}{.1}\right)^n = 2^n$

$\dfrac{Rate\ 2}{Rate\ 1} = \dfrac{4\times10^{-5}Ms^{-1}}{4\times10^{-5}Ms^{-1}} = 1 \Rightarrow 2^n = 1 \Rightarrow n\log 2 = \log 1 \Rightarrow n = \dfrac{\log 1}{\log 2} = 0$

$\dfrac{Exp\ 3}{Exp\ 1} = \dfrac{K(.02)^m(.1)^n}{K(.01)^m(.1)^n} = \dfrac{.02^m}{.01^m} = \left(\dfrac{.02}{.01}\right)^m = 2^m$

$\dfrac{Rate\ 3}{Rate\ 1} = \dfrac{16\times10^{-5}Ms^{-1}}{4\times10^{-5}Ms^{-1}} = 4 \Rightarrow 2^m = 4 \Rightarrow m\log 2 = \log 4 \Rightarrow m = \dfrac{\log 4}{\log 2} = 2$

(b) $Rate = K[A]^2 \Rightarrow K = Rate/[A]^2$

Use data from experiment 1:

$K = \dfrac{4\times10^{-5}Ms^{-1}}{(.01M)^2} = .4\ M^{-1}s^{-1}$

> (a) Rate Law $= .4\ M^{-1}s^{-1}[A]^2$
>
> (b) $K = .4\ M^{-1}s^{-1}$

5) Calculate the pH and the pOH of a 0.050M HClO; Ka of HClO is 3.5448x10^{-8}. Show your calculation with ICE chart (if necessary). (6 pts.)

5) _____

$HClO_{(aq)} + H_2O_{(l)} \rightleftharpoons ClO^-_{(aq)} + H_3O^+_{(aq)}$

	HClO	ClO$^-$	H$_3$O$^+$
I	.05	0	0
C	-X	+X	+X
E	.05-X	X	X

$K_a = \dfrac{[ClO^-][H_3O^+]}{[HClO]} = 3.5448\times10^{-8}$

$K_a = \dfrac{[ClO^-][H_3O^+]}{[HClO]} = \dfrac{(X)(X)}{.05-X} = 3.5448\times10^{-8}$

Because $[HClO]_0 > 100\cdot K_a$ $(.05 > 3.5\times10^{-6})$, I can neglect x in the denominator and use the approximate expression.

$\dfrac{X^2}{.05} = 3.5448\times10^{-8}$

$X^2 = 3.5448\times10^{-8}(.05)$

$X^2 = 1.77\times10^{-9}$

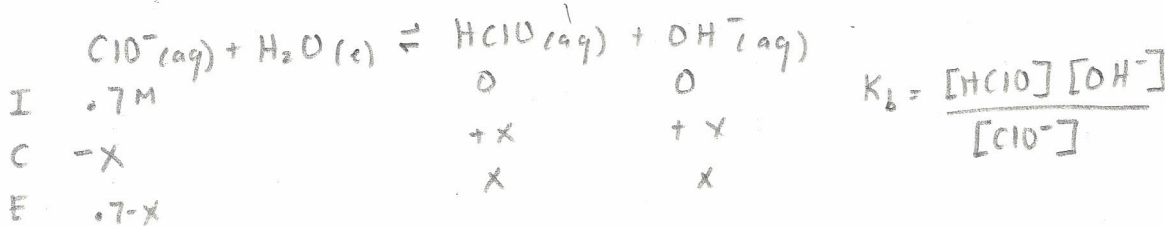$X = \sqrt{1.77\times10^{-9}} = 4.21\times10^{-5}M$

$[H_3O^+] = X = 4.21\times10^{-5}M$

$pH = -\log[H_3O^+] = -\log(4.21\times10^{-5}) = 4.38$

$pH + pOH = 14$

$pOH = 14 - pH \Rightarrow 14 - 4.38 = 9.62$

> $pH = 4.38 \ ; \ pOH = 9.62$

3

6) Calculate the pH of a 0.7M NaClO solution. For your calculation show what happens   6) _____
in a stepwise fashion . Ka of HClO is 3.448×10^{-8} (8 pt.)

NaClO is a sodium salt, so it dissociates completely into Na^+ and ClO^- ions in solution. Hence, $[NaClO] = [Na^+] = [ClO^-]_0 = .7M$

$$ClO^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HClO_{(aq)} + OH^-_{(aq)}$$

I	.7M	0	0
C	−X	+X	+X
		X	X
E	.7−X		

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]}$$

We have Ka of HClO. $HClO_{(aq)} + H_2O_{(\ell)} \rightleftharpoons ClO^-_{(aq)} + H_3O^+$. Since ClO^- is the conjugate base of HClO, we can calculate K_b from the given Ka.

$$Ka \cdot K_b = K_w$$

$$K_b = \frac{K_w}{Ka} = \frac{1 \times 10^{-14}}{3.448 \times 10^{-8}} = 2.9 \times 10^{-7}$$

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = \frac{(x)(x)}{(.7-x)} = 2.9 \times 10^{-7}$$

Because $[ClO^-]_0 > 100 \cdot K_b$ $(.7 > 2.9 \times 10^{-5})$, we can neglect x in the denominator.

$$\frac{x^2}{.7} = 2.9 \times 10^{-7}$$

$$x^2 = .7(2.9 \times 10^{-7}) = 2.03 \times 10^{-7}$$

$$x = \sqrt{2.03 \times 10^{-7}} = 4.51 \times 10^{-4} M$$

$$[OH^-] = x = 4.51 \times 10^{-4} M$$

$$pOH = -\log[OH^-] = -\log[4.51 \times 10^{-4}] = 3.35$$

$$pH + pOH = 14$$

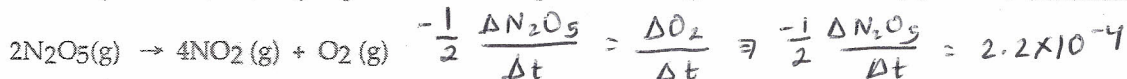$$pH = 14 - pOH \Rightarrow 14 - 3.35 = 10.65$$

$$\boxed{pH = 10.65}$$

4

MULTIPLE CHOICE. Start on line 7 of your scantron paper. Select the one alternative that best completes the statement or answers the question (3 pts each).

7) At elevated temperatures, dinitrogen pentoxide decomposes to nitrogen dioxide and oxygen: 7) _____

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

$-\dfrac{1}{2}\dfrac{\Delta N_2O_5}{\Delta t} = \dfrac{\Delta O_2}{\Delta t}$ ∋ $-\dfrac{1}{2}\dfrac{\Delta N_2O_5}{\Delta t} = 2.2 \times 10^{-4}$

When the rate of formation of O_2 is 2.2×10^{-4} M/s, the rate of decomposition of N_2O_5 is

_____ M/s.

A) 1.1×10^{-4} B) 5.5×10^{-4} C) 2.8×10^{-4} D) 2.2×10^{-4} E) 4.4×10^{-4}

8) The rate law for a reaction is   8) _____

$-\dfrac{1}{2}\dfrac{\Delta N_2O_5}{\Delta t} = \dfrac{(2.2\times10^{-4})}{\Delta t}\dfrac{\Delta O_2}{\Delta t}$

rate = k [A][B]^2

Which one of the following statements is false?
A) The reaction is second order overall.
B) k is the reaction rate constant
C) If [B] is doubled, the reaction rate will increase by a factor of 4.
D) The reaction is second order in B.
E) The reaction is first order in A.

9) Under constant conditions, the half-life of a first-order reaction _____.   9) _____
A) is constant
B) does not depend on the initial reactant concentration
C) is the time necessary for the reactant concentration to drop to half its original value
D) can be calculated from the reaction rate constant
E) All of the above are correct.

$.693/k$

10) Given the following reaction at equilibrium at 450.0°C: 10) _____

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
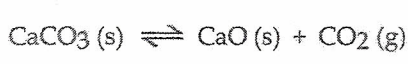
$K_p = P_{CO_2} = .016$

$K_c = [CO_2]$

$K_p = K_c (RT)^{\Delta n}$

$K_p = K_c (RT)^1$

If $pCO_2 = 0.0160$ atm, $K_c =$ _____.

A) 7.23
B) 0.0160
C) 723
D) 0.0821
E) 2.70×10^{-4}

$K_c = \dfrac{K_p}{RT} = \dfrac{.016\,atm}{(723.15)(.0821\frac{atm\cdot L}{mol\cdot K})}$

$K_c = \dfrac{RT}{K_p} = \dfrac{(723.15K)(.0821\frac{atm\cdot L}{mol\cdot K})}{.016\,atm} \cdot \dfrac{L}{mol}$

11) Which solution below has the highest concentration of hydroxide ions?   11) _____
A) pH = 7.00   B) pH = 3.21   C) pH = 7.93   D) pH = 12.6   E) pH = 9.82
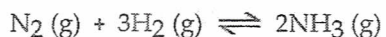
1.62×10^{-11} $.04$

$K_p = K_c (RT)^{\Delta n}$

$K_p = K_c (RT)$

$K_c = \dfrac{K_p}{RT} = \dfrac{.016\,atm}{723.15K\left(\dfrac{.0821\,atm\,L}{mol\cdot K}\right)} = 2.7 \times 10^{-4}$

12) The equilibrium constant for the gas phase reaction

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$$

$$K_{eq} = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$$

is $K_{eq} = 4.34 \times 10^{-3}$ at 300°C. At equilibrium, _____.
A) reactants predominate
B) roughly equal amounts of products and reactants are present
C) products predominate
D) only reactants are present
E) only products are present

12) _____

13) A Brønsted–Lowry base is defined as a substance that _____.
A) acts as a proton donor
B) decreases [H$^+$] when placed in H$_2$O NH_3
C) increases [OH$^-$] when placed in H$_2$O ClO^-
D) increases [H$^+$] when placed in H$_2$O
E) acts as a proton acceptor

13) _____

14) A substance that is capable of acting as both an acid and as a base is _____.
A) saturated
B) autosomal
C) amphoteric
D) conjugated
E) miscible

14) _____

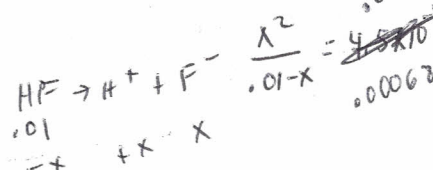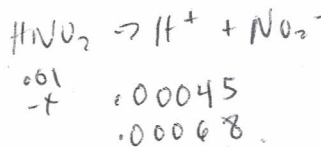15) Classify the following compounds as weak acids (W) or strong acids (S):

HNO_3

benzoic acid   nitric acid   acetic acid

A) S S S   B) S W W   C) W S S   D) W S W   E) W W W

15) _____

16) In which of the following aqueous solutions does the weak acid exhibit the highest percentage ionization?
A) 0.01 M HC$_2$H$_3$O$_2$ (K$_a$ = 1.8 × 10^{-5})
B) 0.01 M HNO$_2$ (K$_a$ = 4.5 × 10^{-4})
C) 0.01 M HClO   (K$_a$ = 3.0 × 10^{-8})
D) 0.01 M HF   (K$_a$ = 6.8 × 10^{-4})
E) These will all exhibit the same percentage ionization.

16) _____

$HNO_2 \to H^+ + NO_2^-$

.01
-t   .00045
        .00068

$HF \to H^+ + F^-$
.01
-t   +x   x

$\dfrac{x^2}{.01-x} = 4.5 \times 10^{-4}$ .00045
.00068

cold   + heat   hot   + heat

$x^2 = $

17) The equilibrium reaction Co(H$_2$O)$_6$$^{2+}$ (aq) (Pink) + 4 Cl$^-$ (aq) <–> CoCl$_4$ $^{2-}$ (aq) (Blue) + 6 H$_2$O(l) turns pink when placed in ice water mixture but turns blue in hot water. The reaction, as shown, is:
A) Insufficient data   B) Nonthermic
C) Endothermic   D) Exothermic

17) _____

$\dfrac{x^2}{.01-x} = .00045$

$\dfrac{x^2}{.01-x} = .00068$

$x^2 = 6.8 \times 10^{-6} - .00068 x$

$x^2 = .000068$

$x^2 + .00068 x - 6.8 \times 10^{-6}$

Pink + heat $\to$ blue

$\dfrac{-.00068 \pm \sqrt{.00068^2 + 4(6.8 \times 10^{-6})}}{2}$

$4.5 \times 10^{-6} = .00045 x + x^2$

$x^2 + .00045 x + 4.5 \times 10^{-6}$

$= .0023 - .00045 \pm \sqrt{(.00045)^2 + 4(4.5 \times 10^{-6})}$

$= .00191$

2   Pink $\to$ Blue + heat