Tutorial

1. Sulfonation of benzene has the following mechanism:

1. $2H_2SO_4 \longrightarrow H_3O^+ + HSO_4^- + SO_3$ (fast)
2. $SO_3 + C_6H_6 \longrightarrow H(C_6H_5^+)SO_3^-$ (slow)
3. $H(C_6H_5^+)SO_3^- + HSO_4^- \longrightarrow C_6H_5SO_3^- + H_2SO_4$ (fast)
4. $C_6H_5SO_3^- + H_3O^+ \longrightarrow C_6H_5SO_3H + H_2O$ (fast)

a. Write an overall equation for the reaction.
b. Write the overall rate law in terms of the initial rate of the reaction.

Plan: The overall reaction can be obtained by adding the three steps together. The overall rate law for the mechanism is determined from the slowest step (the rate-determining step). An overall rate law can only include reactants and products; intermediates cannot be included in the rate law. Express [intermediate] in terms of [reactant].

Solution: Add the steps together and cancel:

$H_2SO_4 + C_6H_6 \rightarrow C_6H_5SO_3H + H_2O$

For the slow step: Rate = $k[SO_3][C_6H_6]$

SO_3 is an intermediate and cannot be included in the overall rate law. SO_3 is produced in step 1 and its concentration is dependent on $k1$ and $[H_2SO_4]$:

$[SO_3] = k_1[H_2SO_4]^2$
Substituting for $[SO_3]$ in the rate law from the slow step: Rate = $k_2\{k_1[H_2SO_4]^2\}[C_6H_6]$
Rate = $k[H_2SO_4]^2[C_6H_6]$

2. Even when a mechanism is consistent with the rate law, later work may show it to be incorrect. For example, the reaction between hydrogen and iodine has this rate law: Rate = $k[H_2][I_2]$. The long-accepted mechanism had a single bimolecular step; that is, the overall reaction was thought to be elementary:

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

In the 1960s, however, spectroscopic evidence showed the presence of free iodine atoms during the reaction. Kineticists have since proposed a three-step mechanism:

$I_2(g) \rightleftharpoons 2I(g)$ (fast)
$H_2(g) + I(g) \rightleftharpoons H_2I(g)$ (fast)
$H_2I(g) + I(g) \longrightarrow 2HI(g)$ (slow)

Show that this mechanism is consistent with the rate law.

Solution:
Rate law for slow step (*Step 3*): Rate = $k_3[H_2I][I]$
Both H_2I and I are intermediates and cannot be in the final rate law.
For an equilibrium, rate forward = rate reverse

From first two steps:
From step 1: $k_1[I_2] = k_{-1}[I]^2$ $[I] = (k_1/k_{-1})^{1/2} [I_2]^{1/2}$
From step 2: $k_2[H_2][I] = k_{-2}[H_2I]$ $[H_2I] = k_2/k_{-2}[H_2][I]$

Substituting in rate = $k_3[H_2I][I]$:

Rate = $k_3[k_2/k_{-2}[H_2][I]][I]$
Rate = $k_3k_2/k_{-2}[H_2][I]^2$

Substituting for [I] in rate = $k_3k_2/k_{-2}[H_2][I]^2$:
Rate = $k_3k_2/k_{-2}(k_1/k_{-1})[H_2][I_2]$ Combining k values:
Rate = $k[H_2][I_2]$ which is consistent with the known rate law.

3. Carbon disulfide, a poisonous flammable liquid, is an excellent solvent for phosphorus, sulfur, and some other nonmetals. A kinetic study of its gaseous decomposition reveals these data:

Experiment	Initial Rate (mol/L·s)	Initial $[CS_2]$ (mol/L)
1	2.7×10^{-7}	0.100
2	2.2×10^{-7}	0.080
3	1.5×10^{-7}	0.055
4	1.2×10^{-7}	0.044

a. Write the rate law for the decomposition of CS_2.
b. Calculate the average value of the rate constant.

Plan: The rate law is rate = $[CS_2]^m$ where *m* is the order of the reactant. To find the order of the reactant, take the ratio of the rate laws for two experiments. Once the rate law is known, any experiment can be used to find the rate constant *k*.
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Solution:

$\text{Rate}_{\text{exp 1}} = \kappa\, [CS_2]_{\text{exp 1}}^{\ m}$

$\text{Rate}_{\text{exp 4}} = \kappa\, [CS_2]_{\text{exp 4}}^{\ m}$

$$\frac{\text{Rate}_{\text{exp 1}}}{\text{Rate}_{\text{exp 4}}} = \left(\frac{[CS_2]_{\text{exp 1}}}{[CS_2]_{\text{exp 4}}}\right)^m$$

2.7x10–7 mol/L•s = (0.100 mol/L)*m* –7 | |
1.2x10 mol/L•s (0.044 mol/L)

2.25 = (2.27273)*m*
log (2.25) = *m* log (2.27273)
m=1
Rate = *k* [CS2]

b) First, calculate the individual *k* values; then average the values.

k = rate/[CS2]

*k*1 = (2.7x10–7 mol/L•s)/(0.100 mol/L) = 2.7x10–6 s–1
*k*2 = (2.2x10–7 mol/L•s)/(0.080 mol/L) = 2.75x10–6 s-1= 2.8x10–6 s–1
*k*3 = (1.5x10–7 mol/L•s)/(0.055 mol/L) = 2.7272x10–6 s-1= 2.7x10–6 s–1
*k*4 = (1.2x10–7 mol/L•s)/(0.044 mol/L) = 2.7272x10–6 s-1= 2.7x10–6 s–1

k_{avg} = [(2.7x10–6 s–1) + (2.75x10–6 s-1) + (2.7272x10–6 s-1) + (2.7272x10–6 s-1)]/4 = 2.7261 10–6 s-1= **2.7x10–6 s–1**

4. Nitrogen dioxide decomposes according to the following reaction, where $K = 4.48 \times 10^{-13}$ at a certain temperature:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

If 0.75 bar of NO_2 is added to a container and allowed to come to equilibrium, what are the equilibrium partial pressures of $NO(g)$ and $O_2(g)$

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ There is a 2:2:1 mole ratio between reactants and products.

Pressure (bar)	$2NO_2(g)$	$\rightleftharpoons$	$2NO(g)$	+	$O_2(g)$	
Initial	0.75		0		0	
Change	– 2x		+2x		+x	(2:2:1 mole ratio)
Equilibrium	0.75 – 2x		2x		x	

$$K = 4.48\text{x}10^{-13} = \frac{p_{NO}^2 p_{O_2}}{p_{NO_2}^2} = \frac{(2\text{x})^2(\text{x})}{(0.75 - 2\text{x})^2}$$

Assume 0.75 bar – 2x ≈ 0.75 bar

$$4.48\text{x}10^{-13} = \frac{(4\text{x}^2)(\text{x})}{(0.75)^2} = \frac{(4\text{x}^3)}{(0.75)^2}$$

x = $3.979\text{x}10^{-5}$ bar = **$4.0\text{x}10^{-5}$ bar O_2** (assumption is justified)

p_{NO} = 2x = 2($3.979\text{x}10^{-5}$ bar) = $7.958\text{x}10^{-5}$ bar = **$8.0\text{x}10^{-5}$ bar NO**

5. A toxicologist studying mustard gas, $S(CH_2CH_2Cl)_2$, a blistering agent, prepares a mixture of 0.675 mol/L SCl_2 and 0.973 mol/L C_2H_4 and allows it to react at room temperature (20.0°C):

$$SCl_2(g) + 2C_2H_4(g) \rightleftharpoons S(CH_2CH_2Cl)_2(g)$$

At equilibrium, $[S(CH_2CH_2Cl)_2]$ = 0.350 mol/L. Calculate *K*.

Concentration (mol/L)	$SCl_2(g)$	+	$2C_2H_4(g)$	$\rightleftharpoons$	$S(CH_2CH_2Cl)_2(g)$
Initial	0.675		0.973		0
Change	– x		– 2x		+x
Equilibrium	0.675 – x		0.973 – 2x		x

$[S(CH_2CH_2Cl)_2]_{eq}$ = x = 0.350 mol/L

$[SCl_2]_{eq}$ = 0.675 – x = 0.675 – 0.350 = 0.325 mol/L

$[C_2H_4]_{eq}$ = 0.973 – 2x = 0.973 – 2(0.350) = 0.273 mol/L

$$K_c = \frac{[S(CH_2CH_2Cl)_2]}{[SCl_2][C_2H_4]^2} = \frac{(0.350)}{(0.325)(0.273)^2} = 14.4497$$

$K = K_c(RT)^{\Delta n}$ Δn = 1 mol – 3 mol = –2

$K = (14.4497)[(0.08314)(273.2 + 20.0)]^{-2}$ = 0.0237617 = **0.0238**

5. Le Châtelier's principle is related ultimately to the rates of the forward and reverse steps in a reaction. Explain (a) why an increase in reactant concentration shifts the equilibrium position to the right, but does not change K; (b) why a decrease in V shifts the equilibrium position toward fewer moles of gas, but does not change K; (c) why a rise in T shifts the equilibrium position of an exothermic reaction toward reactants and also changes K; and (d) why a rise in temperature of an endothermic reaction from T_1 to T_2 results in K_2 being larger than K_1.

a) $Rate_f = k_f[reactants]^x$. An increase in reactant concentration shifts the equilibrium to the right by increasing the initial forward rate. Since $K_{eq} = k_f / k_r$ and k_f and k_r are not changed by changes in concentration, K_{eq} remain constant.
b) A decrease in volume causes an increase in concentrations of gases. The reaction rate for the formation of fewer moles of gases is increased to a greater extent. Again, the k_f and k_r values are unchanged.
c) An increase in temperature increases k_r to a greater extent for an exothermic reaction and thus lowers the K_e value.

6. You are a member of a research team of chemists discussing plans for a plant to produce ammonia:

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

(a) The plant will operate at close to 700 K, at which K is 1.00×10^{-4}, and use the stoichiometric 1/3 ratio of N_2/H_2. At equilibrium, the partial pressure of NH_3 is 50. bar. Calculate the partial pressures of each reactant and p_{total}.

(b) One member of the team has the following suggestion: since the partial pressure of H_2 is cubed in the reaction quotient, the plant could produce the same amount of NH_3 if the reactants were in a 1/6 ratio of N_2/H_2 and could do so at a lower pressure, which would cut operating costs. Calculate the partial pressure of each reactant and p_{total} under these conditions, assuming an unchanged partial pressure of 50. bar for NH_3. Is the suggestion valid

a) $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ The mole ratio $H_2:N_2 = 3:1$; at equilibrium, if $N_2 = x$, $H_2 = 3x$;

$p_{NH_3} = 50.$ bar

$$K = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = 1.00 \times 10^{-4}$$

$$K = \frac{(50.)^2}{(x)(3x)^3} = 1.00 \times 10^{-4}$$

x = 31.02016 = **31 bar N_2**

3x = 3(31.02016) = 93.06049 = **93 bar H_2**

$p_{total} = p_{nitrogen} + p_{hydrogen} + p_{ammonia}$ = (31.02016 bar) + (93.06049 bar) + (50. bar)

= 174.08065 bar= **174 bar total**

b) The mole ratio $H_2:N_2 = 6:1$; at equilibrium, if $N_2 = x$, $H_2 = 6x$; $p_{NH_3} = 50.$ bar

$$K = \frac{(50.)^2}{(x)(6x)^3} = 1.00 \times 10^{-4}$$

x = 18.445 = **18 bar N_2**

6x = 6(18.445) = 110.67 = **111 bar H_2**

$p_{total} = p_{nitrogen} + p_{hydrogen} + p_{ammonia}$ = (18.445 bar) + (110.67 bar) + (50. bar)

= 179.115 bar= **179 bar total**

This is not a valid argument. The total pressure in b) is greater than in a) to produce the same amount of NH_3.

7. In a study of the water-gas shift reaction (see Problem 15.37), equilibrium was reached with [CO] = [H_2O] = [H_2] = 0.10 mol/L and [CO_2] = 0.40 mol/L. After 0.60 mol of H_2 was added to the 2.0-L container and equilibrium was re-established, what were the new concentrations of all the components

Calculate K_c.

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.40)(0.10)}{(0.10)(0.10)} = 4.0$$

Calculate new concentrations.

New H_2 = 0.10 mol/L + (0.60 mol/2.0 L) = 0.40 mol/L

Concentration (mol/L)	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
Initial	0.10	0.10	0.40	0.40
Change	+x	+x	–x	–x
Equilibrium	0.10 + x	0.10 + x	0.40 – x	0.40 – x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.40 - x)(0.40 - x)}{(0.10 + x)(0.10 + x)} = \frac{(0.40 - x)^2}{(0.10 + x)^2} = 4.0 \text{ (take the sq root of both sides)}$$

$$\frac{(0.40 - x)}{(0.10 + x)} = 2.0$$

x = 0.066667

$[CO] = [H_2O]$ = 0.10 + x = 0.10 + 0.066667 = 0.166667 = **0.17 mol/L**

$[CO_2] = [H_2]$ = 0.40 – x = 0.40 – 0.066667 = 0.333333 = **0.33 mol/L**

8. Three beakers contain 100. mL of 0.10 mol/L HCl, $HClO_2$, and HClO, respectively.

   a. Find the pH of each solution.
   b. Describe quantitatively how to make the pH equal in the solutions through the addition of water only.

a) pH = –log [H^+]
HCl is a strong acid so [H^+] = mol/L HCl

pH = –log (0.10) = **1.00**

$HClO_2$ and HClO are weak acids requiring a K_a from the Appendix.

$$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$$

0.10 – x x x

$$K_a = 2.9\text{x}10^{-8} = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

$$K_a = 2.9\text{x}10^{-8} = \frac{(x)(x)}{(0.10 - x)}$$ Assume x is small compared to 0.10.

$$K_a = 2.9\text{x}10^{-8} = \frac{(x)(x)}{(0.10)}$$

[H^+] = x = 5.38516x10^{-5} mol/L
Check assumption: (5.38516x10^{-5}/0.10) x 100% = 0.05%. The assumption is good.
pH = –log [H^+] = –log (5.38516x10^{-5}) = 4.2688 = **4.27**

$$HClO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_2^-(aq)$$

0.10 – x x x

$$K_a = 1.1\text{x}10^{-2} = \frac{[H_3O^+][ClO_2^-]}{[HClO_2]}$$

$$K_a = 1.1\text{x}10^{-2} = \frac{[x][x]}{[0.10 - x]}$$ Assume x is small compared to 0.10.

$$K_a = 1.1\text{x}10^{-2} = \frac{[x][x]}{[0.10]}$$

x = 0.033166
Check assumption: (0.033166/0.10) x 100% = 33%. The assumption is not valid.
The problem will need to be solved as a quadratic.
$x^2 = (1.1\text{x}10^{-2})(0.10 - x) = 1.1\text{x}10^{-3} - 1.1\text{x}10^{-2}\,x$
$x^2 + 1.1\text{x}10^{-2}\,x - 1.1\text{x}10^{-3} = 0$
a = 1 b = 1.1x10^{-2} c = – 1.1x10^{-3}

$$x = \frac{-1.1\text{x}10^{-2} \pm \sqrt{(1.1\text{x}10^{-2})^2 - 4(1)(-1.1\text{x}10^{-3})}}{2(1)}$$

x = 2.8119x10^{-2} mol/L H^+
pH = –log [H^+] = –log (2.8119x10^{-2}) = 1.550997 = **1.55**

b) The lowest H^+ concentration is from the HClO. Leave the HClO beaker alone, and dilute the other acids until they yield the same H^+ concentration. A dilution calculation is needed to calculate the amount of water added.

HCl c_i = 0.10 mol/L V_i = 100. mL c_f = 5.38516x10^{-5} mol/L V_f = ?
$c_iV_i = c_fV_f$
$V_f = c_iV_i/c_f$ = [(0.10 mol/L)(100. mL)]/(5.38516x10^{-5} mol/L) = 1.85695x10^5 mL
Volume water added = (1.85695x10^5 mL) – 100. mL = 1.85595x10^5 = **1.9x10^5 mL H_2O added**

$HClO_2$ requires the K_a for the acid with the ClO_2^- concentration equal to the H_3O^+ concentration. The final concentration (mol/L) of the acid will be c_f, which may be used in the dilution equation.

$$HClO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_2^-(aq)$$

x – 5.38516x10^{-5} 5.38516x10^{-5} 5.38516x10^{-5}

$$K_a = 1.1\text{x}10^{-2} = \frac{[H_3O^+][ClO_2^-]}{[HClO_2]}$$

$$K_a = 1.1\text{x}10^{-2} = \frac{[5.38516\text{x}10^{-5}][5.38516\text{x}10^{-5}]}{[x - 5.38516\text{x}10^{-5}]}$$

x = M_f = 5.41152x10^{-5} mol/L

c_i = 0.10 mol/L V_i = 100. mL c_f = 5.41152x10^{-5} mol/L V_f = ?
$c_iV_i = c_fV_f$
$V_f = c_iV_i/c_f$ = [(0.10 mol/L)(100. mL)]/(5.41152x10^{-5} mol/L) = 1.8479x10^5 mL
Volume water added = (1.8479x10^5 mL) – 100. mL = 1.8469x10^5 mL= **1.8x10^5 mL H_2O added**

9. An industrial chemist who is studying bleaching and sterilizing prepares several hypochlorite buffers. Find the pH of (a) 0.100 mol/L HClO and 0.100 mol/L NaClO; (b) 0.100 mol/L HClO and 0.150 mol/L NaClO; (c) 0.150 mol/L HClO and 0.100 mol/L NaClO; (d) 1.0 L of the solution in part (a) after 0.0050 mol of NaOH has been added.

The value of the K_a from the Appendix: $K_a = 2.9\text{x}10^{-8}$

$pK_a = -\log(2.9\text{x}10^{-8}) = 7.5376$

$$pH = pK_a + \log\left(\frac{[ClO^-]}{[HClO]}\right)$$

a) $pH = 7.5376 + \log\left(\frac{[0.100]}{[0.100]}\right) = 7.5376 = \mathbf{7.54}$

b) $pH = 7.5376 + \log\left(\frac{[0.150]}{[0.100]}\right) = 7.71369 = \mathbf{7.71}$

c) $pH = 7.5376 + \log\left(\frac{[0.100]}{[0.150]}\right) = 7.3615 = \mathbf{7.36}$

d) The reaction is $NaOH + HClO \rightarrow Na^+ + ClO^- + H_2O$.

The original amount (mol) of HClO and OCl^- are both = (0.100 mol/L)(1.0 L) = 0.100 mol

	$NaOH$	+	$HClO$	$\rightarrow$	Na^+	+	ClO^-	+	H_2O
Initial	0.0050 mol		0.100 mol				0.100 mol		
Change	–0.0050 mol		–0.0050 mol				+ 0.0050 mol		
Final	0 mol		0.095 mol				0.105 mol		

$pH = 7.5376 + \log\left(\frac{[0.105]}{[0.095]}\right) = 7.5811 = \mathbf{7.58}$

10. Find the pH during the titration of 20.00 mL of 0.1000 mol/L triethylamine, $(CH_3CH_2)_3N$ ($K_b = 5.2 \times 10^{-4}$), with 0.1000 mol/L HCl solution after each of the following additions of titrant:

0 mL
10.00 mL
15.00 mL
19.00 mL
19.95 mL
20.00 mL
20.05 mL
25.00 mL

This is a titration between a weak base and a strong acid. The pH before addition of the acid is dependent on the K_b of the base ($(CH_3CH_2)_3N$). Prior to reaching the equivalence point, the added acid reacts with base to form $(CH_3CH_2)_3NH^+$ ion. The equivalence point occurs when 20.00 mL of acid is added to the base because at this point, amount (mol) acid = amount (mol) base. Addition of acid beyond the equivalence point is simply the addition of excess H_3O^+.

The initial amount (mol) of $(CH_3CH_2)_3N$ = (0.1000 mol $(CH_3CH_2)_3N$)/L)(10^{-3} L/1 mL)(20.00 mL)

= $2.000\text{x}10^{-3}$ mol $(CH_3CH_2)_3N$

a) Since no acid has been added, only the weak base (K_b) is important.

$$K_b = 5.2\text{x}10^{-4} = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{(x)(x)}{(0.1000 - x)} = \frac{(x)(x)}{(0.1000)}$$

$[OH^-] = x = 7.2111\text{x}10^{-3}$ mol/L

$pOH = -\log(7.2111\text{x}10^{-3}) = 2.141998$

$pH = 14.00 - pOH = 14.00 - 2.141998 = 11.8580 =$ **11.86**

b) Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(10.00 mL) = $1.000\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and $1.000\text{x}10^{-3}$ mol $(CH_3CH_2)_3N$ will remain; an equal amount (mol) of $(CH_3CH_2)_3NH^+$ will form.

The volume of the solution at this point is [(20.00 + 10.00) mL](10^{-3} L/1 mL) = 0.03000 L

The concentration (mol/L) of the excess $(CH_3CH_2)_3N$ is

($1.000\text{x}10^{-3}$ mol $(CH_3CH_2)_3N$)/(0.03000 L) = 0.03333 mol/L

The concentration (mol/L) of the $(CH_3CH_2)_3NH^+$ formed is

($1.000\text{x}10^{-3}$ mol $(CH_3CH_2)_3NH^+$)/(0.03000 L) = 0.03333 mol/L

$$K_b = 5.2\text{x}10^{-4} = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{(x)(0.0333+x)}{(0.03333-x)} = \frac{(x)(0.0333)}{(0.03333)}$$

$[OH^-] = x = 5.2\text{x}10^{-4}$ mol/L

$pOH = -\log(5.2\text{x}10^{-4}) = 3.283997$

$pH = 14.00 - pOH = 14.00 - 3.283997 = 10.7160 =$ **10.72**

c) Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(15.00 mL) = $1.500\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and $5.00\text{x}10^{-4}$ mol $(CH_3CH_2)_3N$ will remain; and $1.500\text{x}10^{-3}$ moles of $(CH_3CH_2)_3NH^+$ will form.

The volume of the solution at this point is [(20.00 + 15.00) mL](10^{-3} L/1 mL) = 0.03500 L

The concentration (mol/L) of the excess $(CH_3CH_2)_3N$ is

($5.00\text{x}10^{-4}$ mol $(CH_3CH_2)_3N$)/(0.03500 L) = 0.0142857 mol/L

The concentration (mol/L) of the $(CH_3CH_2)_3NH^+$ formed is

($1.500\text{x}10^{-3}$ mol $(CH_3CH_2)_3NH^+$)/(0.03500 L) = 0.0428571 mol/L

$$K_b = 5.2\text{x}10^{-4} = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{(x)(0.0428571+x)}{(0.0142857-x)} = \frac{(x)(0.0428571)}{(0.0142857)}$$

$[OH^-] = x = 1.7333\text{x}10^{-4}$ mol/L

$pOH = -\log(1.7333\text{x}10^{-4}) = 3.761126$

$pH = 14.00 - pOH = 14.00 - 3.761126 = 10.23887 =$ **10.24**

d) Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(19.00 mL) = $1.900\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and $1.00\text{x}10^{-4}$ mol $(CH_3CH_2)_3N$ will remain; and $1.900\text{x}10^{-3}$ moles of $(CH_3CH_2)_3NH^+$ will form.

The volume of the solution at this point is [(20.00 + 19.00) mL](10^{-3} L/1 mL) = 0.03900 L

The concentration (mol/L) of the excess $(CH_3CH_2)_3N$ is

($1.00\text{x}10^{-4}$ mol $(CH_3CH_2)_3N$)/(0.03900 L) = 0.002564103 mol/L

The concentration (mol/L) of the $(CH_3CH_2)_3NH^+$ formed is

($1.900\text{x}10^{-3}$ mol $(CH_3CH_2)_3NH^+$)/(0.03900 L) = 0.0487179 mol/L

$$K_b = 5.2\text{x}10^{-4} = \frac{\left[(CH_3CH_2)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_3N\right]} = \frac{(x)(0.0487179 + x)}{(0.002564103 - x)} = \frac{(x)(0.0487179)}{(0.002564103)}$$

$[OH^-] = x = 2.73684\text{x}10^{-5}$ mol/L

$pOH = -\log(2.73684\text{x}10^{-5}) = 4.56275$

$pH = 14.00 - pOH = 14.00 - 4.56275 = 9.43725 =$ **9.44**

e) Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(19.95 mL) = $1.995\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and $5\text{x}10^{-6}$ mol $(CH_3CH_2)_3N$ will remain; and $1.995\text{x}10^{-3}$ moles of $(CH_3CH_2)_3NH^+$ will form.

The volume of the solution at this point is [(20.00 + 19.95) mL](10^{-3} L/1 mL) = 0.03995 L

The concentration (mol/L) of the excess $(CH_3CH_2)_3N$ is

($5\text{x}10^{-6}$ mol $(CH_3CH_2)_3N$)/(0.03995 L) = 0.000125156 mol/L

The concentration (mol/L) of the $(CH_3CH_2)_3NH^+$ formed is

$(1.995\text{x}10^{-3}$ mol $(CH_3CH_2)_3NH^+)/(0.03995$ L) = 0.0499374 mol/L

$$K_b = 5.2\text{x}10^{-4} = \frac{[(CH_3CH_2)_3NH^+][OH^-]}{[(CH_3CH_2)_3N]} = \frac{(x)(0.0499374 + x)}{(0.000125156 - x)} = \frac{(x)(0.0499374)}{(0.000125156)}$$

$[OH^-] = x = 1.303254\text{x}10^{-6}$ mol/L

pOH = –log $(1.303254\text{x}10^{-6})$ = 5.88497

pH = 14.00 – pOH = 14.00 – 5.88497 = 8.11503 = **8.1**

f) Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(20.00 mL) = $2.000\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and 0 mol $(CH_3CH_2)_3N$ will remain; and $2.000\text{x}10^{-3}$ moles of $(CH_3CH_2)_3NH^+$ will form. This is the equivalence point.

The volume of the solution at this point is [(20.00 + 20.00) mL](10^{-3} L/1 mL) = 0.04000 L

The concentration (mol/L)of the $(CH_3CH_2)_3NH^+$ formed is

$(2.000\text{x}10^{-3}$ mol $(CH_3CH_2)_3NH^+)/(0.04000$ L) = 0.05000 mol/L

$K_a = K_w/K_b = (1.0\text{x}10^{-14})/(5.2\text{x}10^{-4}) = 1.9231\text{x}10^{-11}$

$$K_a = 1.9231\text{x}10^{-11} = \frac{[H_3O^+][(CH_3CH_2)_3N]}{[(CH_3CH_2)_3NH^+]} = \frac{(x)(x)}{(0.05000 - x)} = \frac{(x)(x)}{(0.05000)}$$

$x = [H_3O^+] = 9.80587\text{x}10^{-7}$ mol/L

pH = –log $[H^+]$ = –log $(9.80587\text{x}10^{-7})$ = 6.0085 = **6.01**

g) After the equivalence point, the excess strong acid is the primary factor influencing the pH.

Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(20.05 mL)

= $2.005\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and 0 mol $(CH_3CH_2)_3N$ will remain, and $5\text{x}10^{-6}$ moles of HCl will be in excess.

The volume of the solution at this point is [(20.00 + 20.05) mL](10^{-3} L/1 mL) = 0.04005 L

The concentration (mol/L) of the excess H^+ is ($5\text{x}10^{-6}$ mol H^+)/(0.04005 L) = $1.2484\text{x}10^{-4}$ mol/L*M*

pH = –log $(1.2484\text{x}10^{-4})$ = 3.9036 = **3.90**

h) Determine the amount (mol) of HCl added:

amount (mol) of added HCl = (0.1000 mol HCl/L)(10^{-3} L/1 mL)(25.00 mL) = $2.500\text{x}10^{-3}$ mol HCl

The HCl will react with an equal amount of the base, and 0 mol $(CH_3CH_2)_3N$ will remain, and $5.00\text{x}10^{-4}$ mol of HCl will be in excess.

The volume of the solution at this point is [(20.00 + 25.00) mL](10^{-3} L/1 mL) = 0.04500 L

The concentration (mol/L) of the excess H^+ is ($5.00\text{x}10^{-4}$ mol H^+)/(0.04500 L) = $1.1111\text{x}10^{-2}$ mol/L

pH = –log $(1.1111\text{x}10^{-2})$ = 1.9542 = **1.95**

10. Does any solid Ag_2CrO_4 form when 2.7×10^{-5} g of $AgNO_3$ is dissolved in 15.0 mL of 4.0×10^{-4} mol/L K_2CrO_4?

The ion-product expression for Ag_2CrO_4 is $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$ and, from the Appendix, K_{sp} equals $2.6\text{x}10^{-12}$. To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp}.

$$[Ag^+] = \left(\frac{2.7\text{x}10^{-5}\text{ g } AgNO_3}{15.0\text{ mL}}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)\left(\frac{1\text{ mol } AgNO_3}{169.9\text{ g } AgNO_3}\right)\left(\frac{1\text{ mol } Ag^+}{1\text{ mol } AgNO_3}\right) = 1.0594467\text{x}10^{-5}\text{ mol/L } Ag^+$$

$$[CrO_4^{2-}] = \left(\frac{4.0\text{x}10^{-4}\text{ mol } K_2CrO_4}{L}\right)\left(\frac{1\text{ mol } CrO_4^{2-}}{1\text{ mol } K_2CrO_4}\right) = 4.0\text{x}10^{-4}\text{ mol/L } IO_3^-$$

$Q_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.0594467\text{x}10^{-5})^2(4.0\text{x}10^{-4}) = 4.4897\text{x}10^{-14}$

Since $Q_{sp} < K_{sp}$ ($4.5\text{x}10^{-14} < 2.6\text{x}10^{-12}$), **$Ag_2CrO_4$ will not precipitate**.