Big Idea #6

Big Idea 6: Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external disturbances.

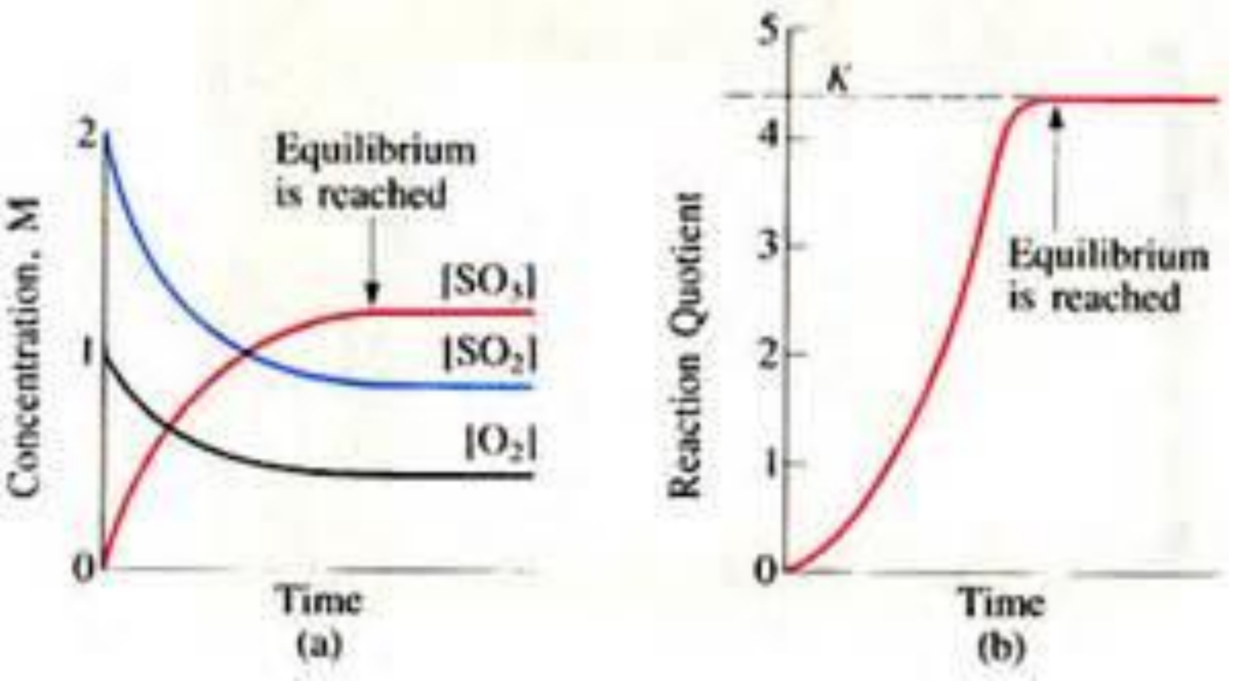
Enduring Understanding

- 6.A: Chemical equilibrium is a dynamic, reversible state in which rates of opposing processes are equal.
- 6.B: Systems at equilibrium are responsive to external disturbances, with the response leading to a change in the composition of the system.
- 6.C: Chemical equilibrium plays an important role in acid-base chemistry and in solubility.
- 6.D: The equilibrium constant is related to temperature and the difference in Gibbs free energy between reactants and products.

Reviewing concepts

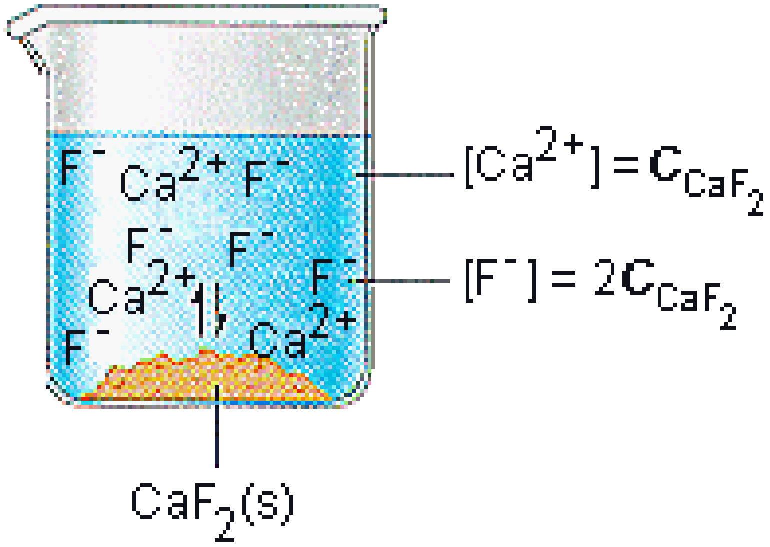
- What is an equilibrium constant and how do I write out the expression.
  - K = [P]/[R]
  - Tracking concentrations. Pure solids and liquids do not have a concentration.
  - All K values are temperature dependent

  - Use coefficients to write out equilibrium expressions



Solubility Equilibrium - Ksp

- $Ag_2SO_{4(s)} \Leftrightarrow 2Ag^+ + S^{2-}$
- $Ksp = [Ag^+]^2[S^{2-}]$



- Notice the difference:
- Molecular equation
  - $AgNO_{3(aq)} + Na_2S_{(aq)} \Leftrightarrow AgS_{(s)} + NaNO_{3(aq)}$
- Ionic equation
  - $Ag^+ + NO_3^{-1} + 2Na^+ + S^{-2} \Leftrightarrow AgS_{(s)} + Na^+ + 2NO_3^{-1}$
- Net Ionic
  - $Ag^+ + 2S^{-2} \Leftrightarrow AgS_{(s)}$

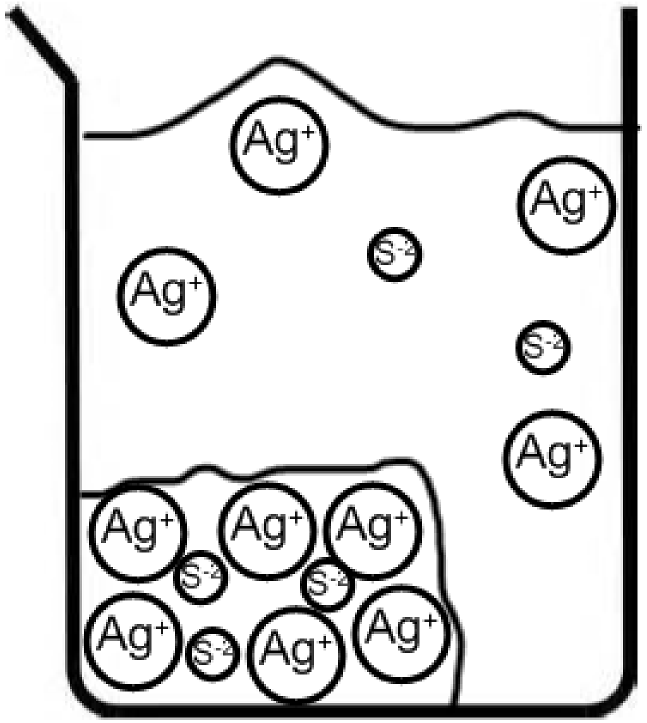
Given Equilibrium concentrations determine K

- $Ag_2S_{(s)} \Leftrightarrow 2Ag^+ + S^{2-}$
- $Ksp = [Ag^+]^2[S^{2-}]$

- Given the molar solubility of Ag_2S is .005M at some temperature.
- Be able to draw a picture of such a solution
- Determine the concentration of each ion.
- Determine Ksp.

Draw a picture

- Notice:
  - Very often Relative Sizes are important
  - we have ratios of 2:1 in the solution
  - Solid on the bottom so solution is saturated



Concentration and Ksp

- $Ag_2S_{(s)} \Leftrightarrow 2Ag^+ + S^{2-}$
- $Ksp = [Ag^+]^2[S^{2-}]$

- $Ag_2S_{(s)} \Leftrightarrow 2Ag^+ + S^{2-}$
- 0.005M is dissolved
- $[Ag^+] = .010M$
- $[S^{2-}] = .0050M$
- $Ksp = [.010]^2[.0050]$
- 0.0000050M

Reaction Quotient: How much can dissolve?

- $Ag_2S_{(s)} \Leftrightarrow 2Ag^+ + S^{2-}$
- $Ksp = [Ag^+]^2[S^{2-}]$

Remember Ksp represent Max solubility.

$[Ag^+]^2[S^{2-}]$ = can not exceed K (only so much room)

Questions:

- If some Ions are already present, how much more room is left?
- If stuff is mixed together will the maximum be reached causing precipitation?

If some Ions are already present, how much more room is left? (common ion effect)

- $Ag_2S_{(s)} \Leftrightarrow 2Ag^+ + S^{2-}$
- $Ksp = [Ag^+]^2[S^{2-}]$

- Dissolve Ag_2S in an aqueous solution of .5M Na_2S
- $Ag_2S_{(s)} \Leftrightarrow 2Ag^+ + S^{2-}$

I	-	0	.5
S	-	+2x	x
E	-	2x	.5+x

$Ksp = [2x]^2[.5]$

Solve for x.

If stuff is mixed together will the maximum be reached causing precipitation?

- Note: If you are mixing volumes than you will need to recalculate new concentrations with new larger volume. (M = mol/l or $M_1V_1 = M_2V_2$)

- Mix together 50mL of .1M Na_2S and 50mL .01M $AgNO_3$
- Answer: Calculate Reaction Q. Substituting in new concentrations and compare to K.
- New Concentrations: In this case volumes are doubled so concentrations are cut in half.
- $Q = [Ag^+]^2[S^{2-}] = [.05]^2[.005] = .0000125$ Compare to K
- If Q > K then reaction will precipitate

Kc vs Kp

- Write out the equilibrium expression for the following reaction using pressures (ATM) instead of molarity.

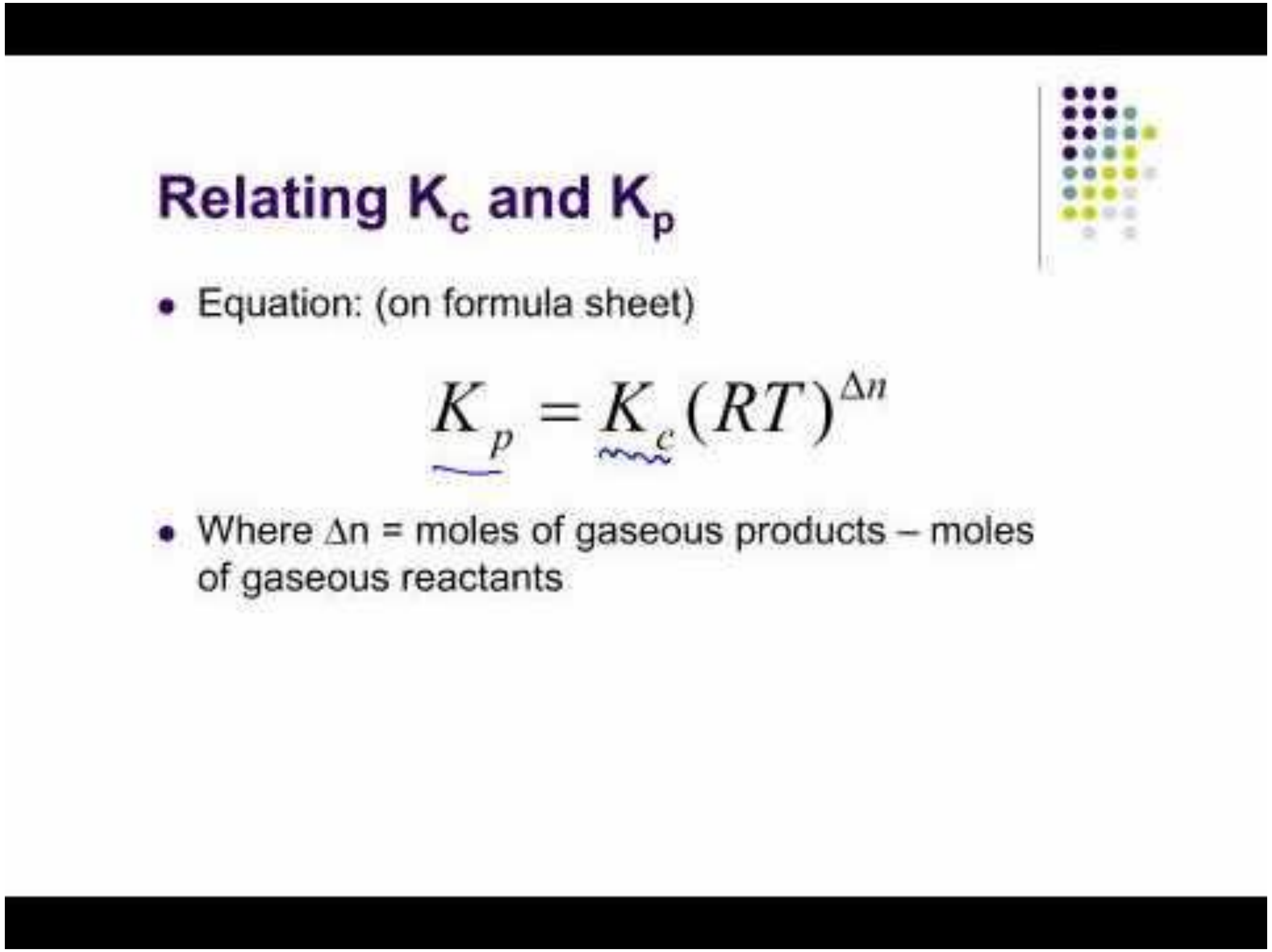
$$X_{(s)} + 2Y_{(aq)} \Leftrightarrow Z_{(l)} + 2W_{(g)}$$

$$Kp = p(w)^2$$

Can you convert Kc to Kp… yes

- This equation is no longer available on the AP Exam.
- Note: If $\Delta n = 0$ then Kc = Kp

- Ex:
- $X_g + Y(s) \Leftrightarrow Z(g)$
- Moles of gas are equal
- Kc = Kp



Acid Base equilibrium

- Strong vs. Weak
  - Strong acids go to completion – **no** K value is needed.
  - Weak acids go to equilibrium – K is needed.

ALL K VALUES ARE USED WITH THE SAME CHEMICAL REACTION: **HYDROLYSIS**

$HX_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + X^-_{(aq)}$ $\quad$ $Ka = [H_3O^+][X^-]/[HX]$

$X^-_{(aq)} + H_2O_{(l)} \Leftrightarrow OH^-_{(aq)} + HX_{(aq)}$ $\quad$ $Kb = [OH^-][HX]/[X^-]$

Determine pH or $[H^+]$ or $[OH^-]$ from?

$$HX_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + X^-_{(aq)}$$

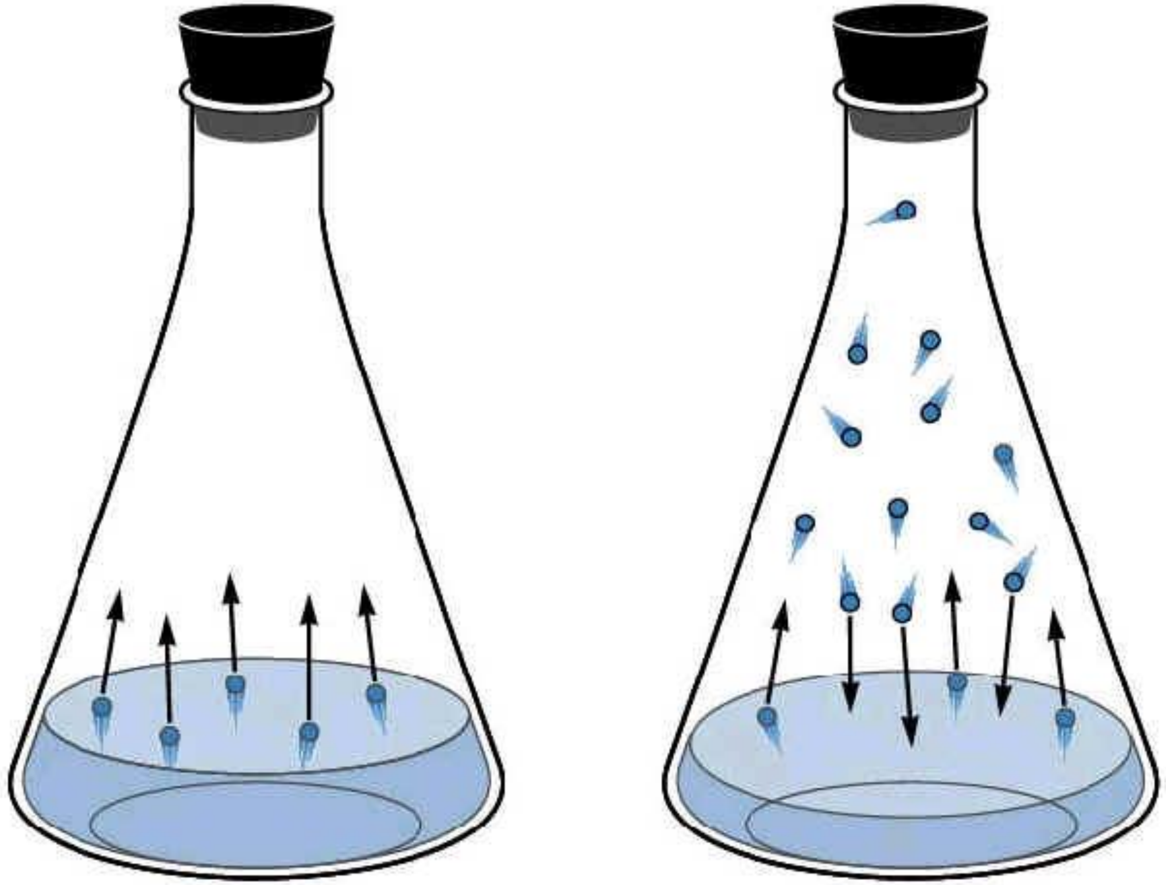
$$Ka = [H_3O^+][X^-]/[HX]$$

	$HX_{(aq)}$	$H_2O_{(l)}$	$H_3O^+_{(aq)}$	$X^-_{(aq)}$
I		-	0	
S	-x	-	+x	+x
E		-		

Notice:

- Anytime you want a K value you must have all E…
- Give I concentrations Find $H_3O^+ \Rightarrow$ pH
- Give pH $\Rightarrow H_3O^+$ determine K value

Vaporization equilibrium



$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$$

7. At 450°C, 2.0 moles each of $H_2(g)$, $I_2(g)$, and $HI(g)$ are combined in a 1.0 L rigid container. The value of K_c at 450°C is 50. Which of the following will occur as the system moves toward equilibrium?

   (A) More $H_2(g)$ and $I_2(g)$ will form.
   (B) More $HI(g)$ will form.
   (C) The total pressure will decrease.
   (D) No net reaction will occur, because the number of molecules is the same on both sides of the equation.

Determine the answer

$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$$

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(C) The total pressure will decrease.
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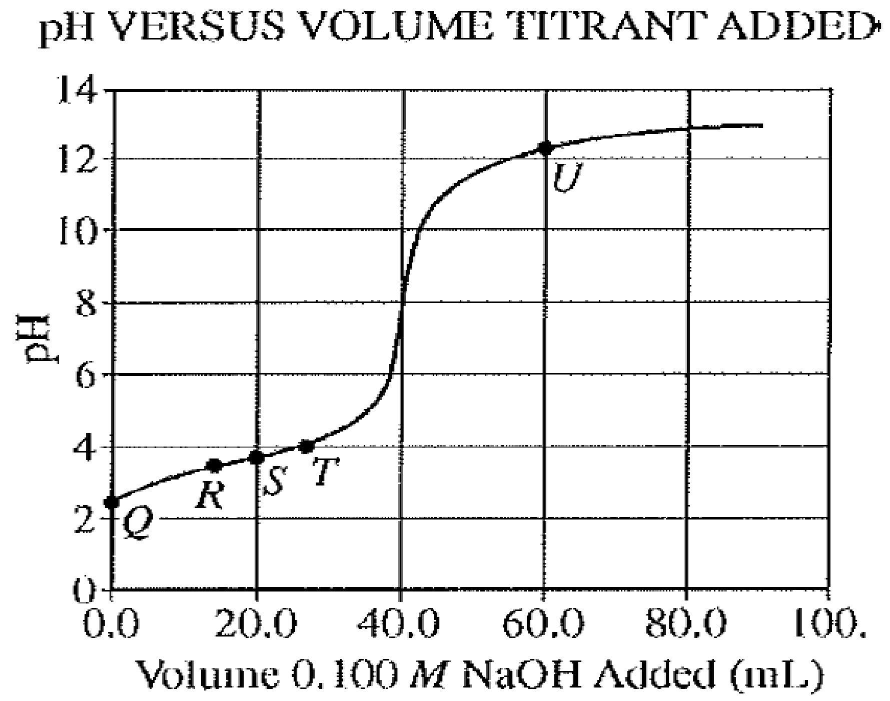
The reaction will shift to equilibrium based upon Q = K.
$Q = (2)^2/(2) * (2) = 1$
Q will need to get bigger which is a shift to more product!

B is correct

Very common set of questions…

Questions 14-17 refer to the following.



A 50.0 mL sample of an acid, HA, of unknown molarity is titrated, and the pH of the resulting solution is measured with a pH meter and graphed as a function of the volume of 0.100 *M* NaOH added.

14. At point *R* in the titration, which of the following species has the highest concentration?

(A) HA

(B) A^-

(C) H_3O^+

(D) OH^-

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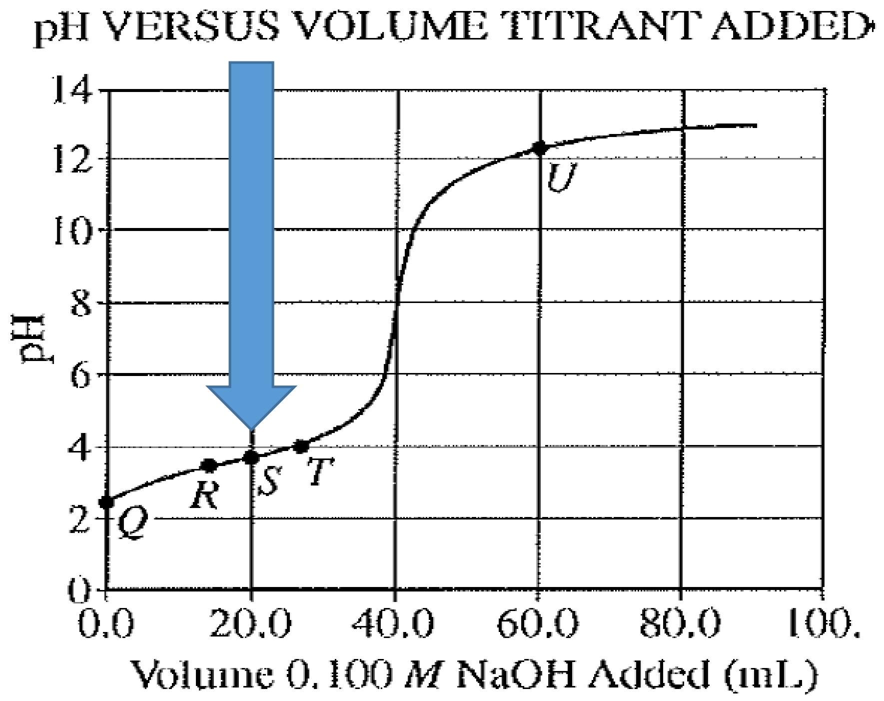

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14. At point *R* in the titration, which of the following species has the highest concentration?

(A) HA

(B) A^-

(C) H_3O^+

(D) OH^-

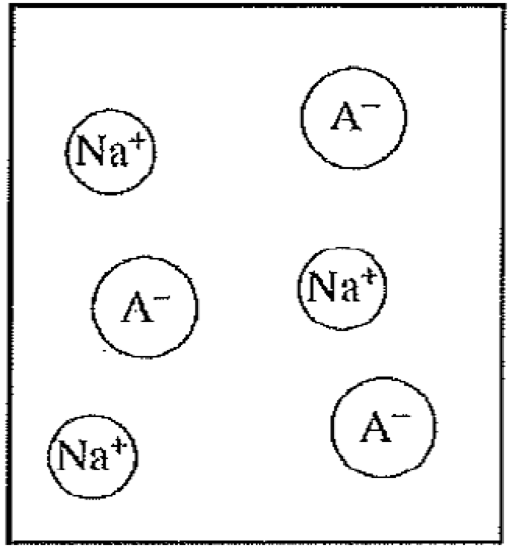
At "S" HA = A^-

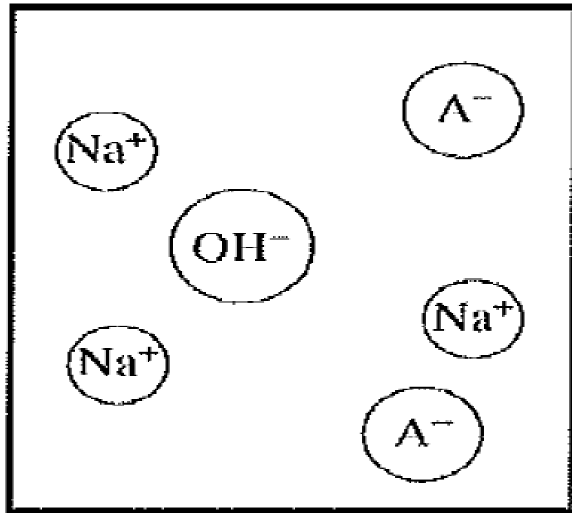
So R has more HA

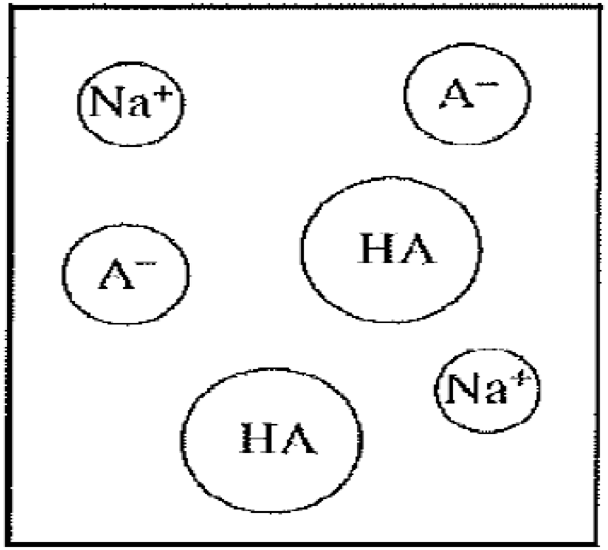
Which of the following is the best particulate representation of the species (other than H_2O) that are present in significant concentrations in the solution at point *U* in the titration?

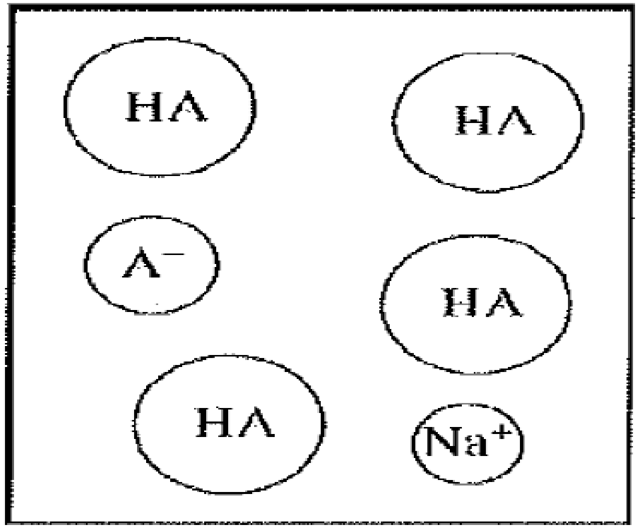
Big Idea 3: Reactions

Not an equilibrium question but goes along with this set so it is included.





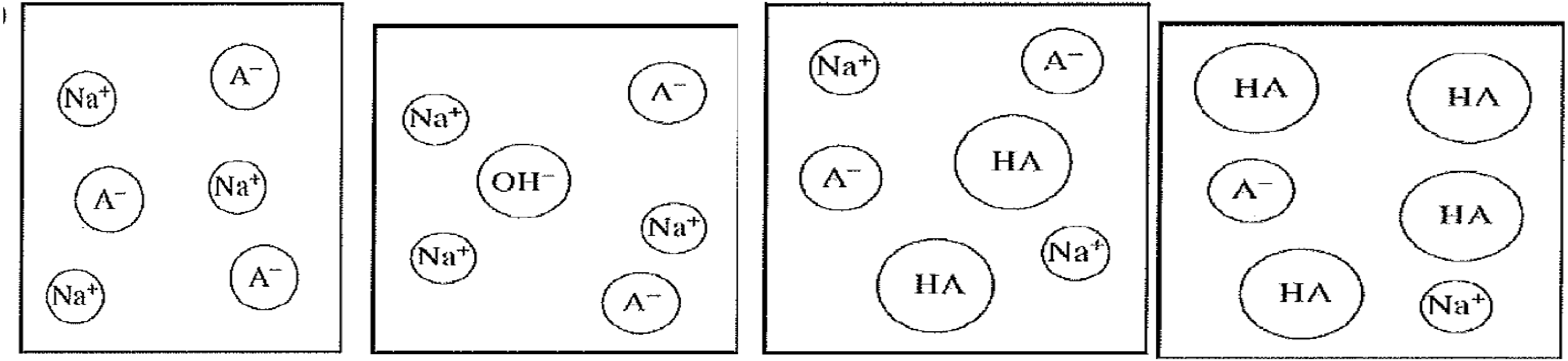




Which of the following is the best particulate representation of the species (other than H_2O) that are present in significant concentrations in the solution at point *U* in the titration?

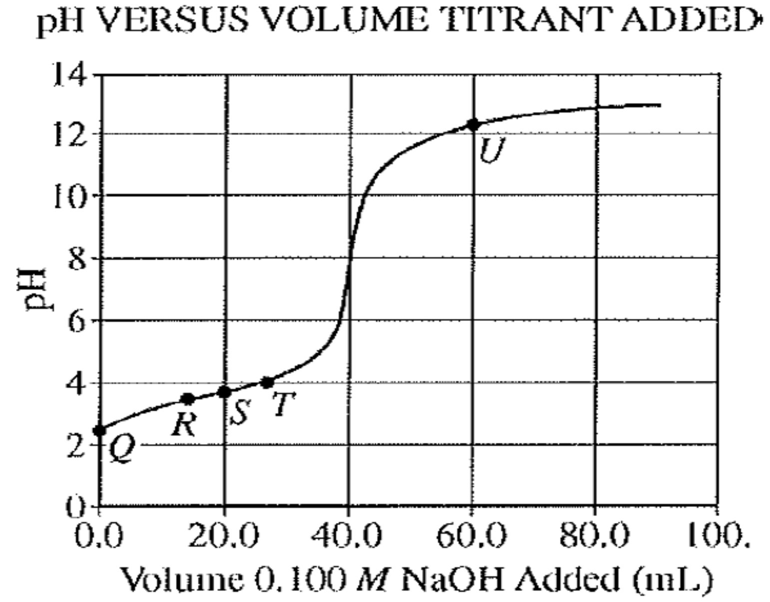
At point U, All HA has been converted to A- and excess OH^- is starting to build up.

B is correct



Big Idea 6

Questions 14-17 refer to the following.



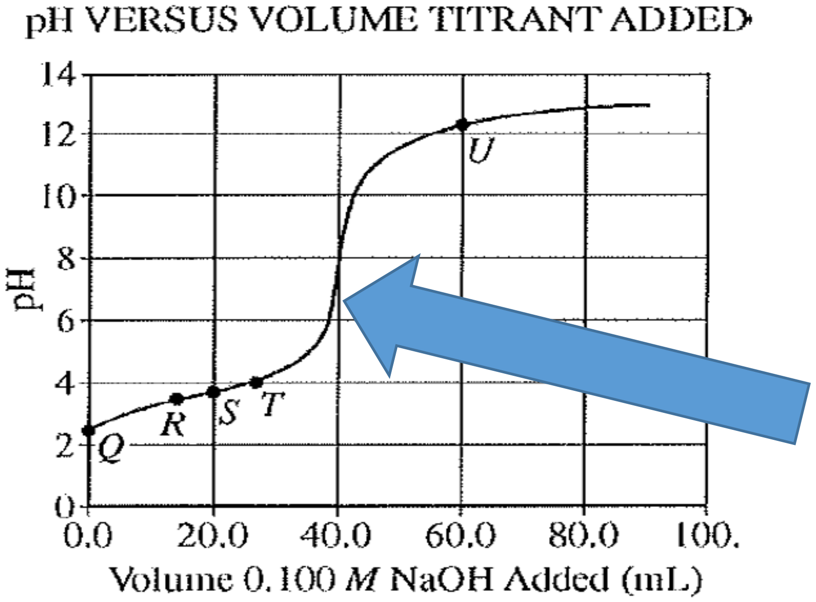
A 50.0 mL sample of an acid, HA, of unknown molarity is titrated, and the pH of the resulting solution is measured with a pH meter and graphed as a function of the volume of 0.100 *M* NaOH added.

16. At which point on the titration curve is $[A^-]$ closest to twice that of [HA] ?

(A) *R*
(B) *S*
(C) *T*
(D) *U*

Big Idea 6

Questions 14-17 refer to the following.



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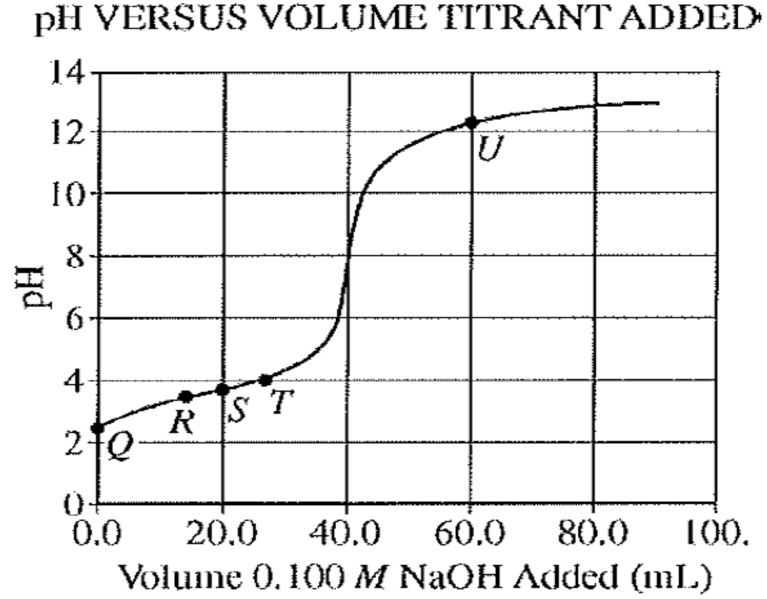
16. At which point on the titration curve is $[A^-]$ closest to twice that of [HA] ?

(A) *R*
(B) *S*
(C) *T*
(D) *U*

Again, One should know that S is half equivalence so at S HA = A^- To answer that question T is the only Logical choice. The arrow I have added is where all HA Is gone.

Big Idea 1

Questions 14-17 refer to the following.



A 50.0 mL sample of an acid, HA, of unknown molarity is titrated, and the pH of the resulting solution is measured with a pH meter and graphed as a function of the volume of 0.100 *M* NaOH added.

17. A student carries out the same titration, but uses an indicator instead of a pH meter. If the indicator changes color slightly past the equivalence point, what will the student obtain for the calculated concentration of the acid?

(A) Slightly less than 0.0800 *M*
(B) Slightly more than 0.0800 *M*
(C) Slightly less than 0.125 *M*
(D) Slightly more than 0.125 *M*

Big Idea 1

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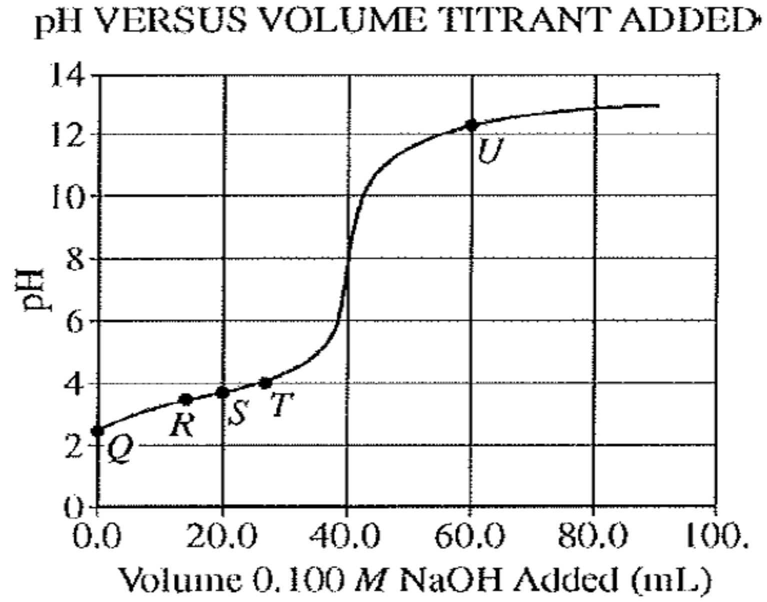

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(A) Slightly less than 0.0800 *M*
(B) Slightly more than 0.0800 *M* ←
(C) Slightly less than 0.125 *M*
(D) Slightly more than 0.125 *M*

This is a proportional question: Notice it takes 50 mL of unknown HA to reach equivalence with 40 mL of NaOH.

Moles are equal/Larger volume = .08 and not .125

Error occurred causing more moles to be added which raises the 0.08
To a value of larger then 0.08
B = the answer

Determine the answer

22. Caffeine ($C_8H_{10}N_4O_2$) is a weak base with a K_b value of 4×10^{-4}. The pH of a 0.01 *M* solution of caffeine is in the range of

(A) 2–3
(B) 5–6
(C) 7–8
(D) 11–12

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(B) 5–6
(C) 7–8
(D) 11–12

You can do all the math but this is a weak base and therefore there is only 1 pH range that included pH of a weak base. Answer is D

See next slide for calculation.

Mathematical justification for answer A

22. Caffeine ($C_8H_{10}N_4O_2$) is a weak base with a K_b value of 4×10^{-4}. The pH of a 0.01 *M* solution of caffeine is in the range of

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- $X^- + H_2O \Leftrightarrow HX + OH^-$

I	.01	-	0	0
S	-x	-	+x	+x
E	.01 –x		x	x

4E-4 = X^2/.01

Lets do the math… no calculator

.04 E-4 = X^2 or .000004 = x^2

X = .002 (.log of .001 = 3 and we are larger so we will be more basic. Although very close 2.68 is still must be less than 3. and this is the pOH so the pH is nearly 11

Answer is D

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$$

$PCl_5(g)$ decomposes into $PCl_3(g)$ and $Cl_2(g)$ according to the equation above. A pure sample of $PCl_5(g)$ is placed in a rigid, evacuated 1.00 L container. The initial pressure of the $PCl_5(g)$ is 1.00 atm. The temperature is held constant until the $PCl_5(g)$ reaches equilibrium with its decomposition products. The figures below show the initial and equilibrium conditions of the system.

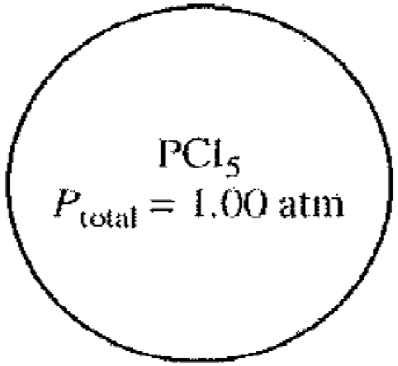

Figure 1: Initial

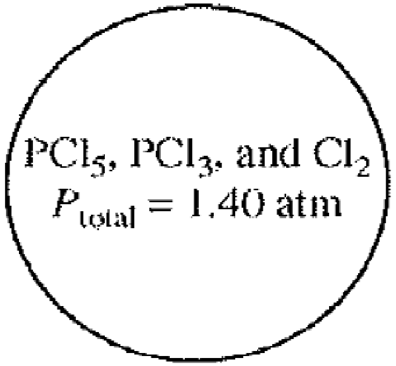

Figure 2: Equilibrium

30. As the reaction progresses toward equilibrium, the rate of the forward reaction

(A) increases until it becomes the same as the reverse reaction rate at equilibrium
(B) stays constant before and after equilibrium is reached
(C) decreases to become a constant nonzero rate at equilibrium
(D) decreases to become zero at equilibrium

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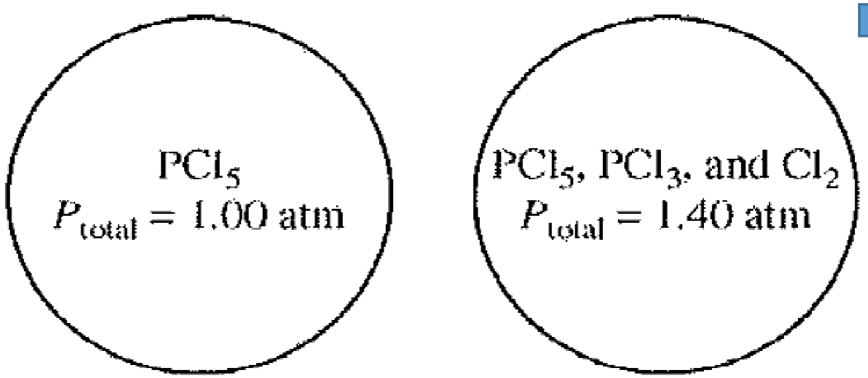

Figure 1: Initial Figure 2: Equilibrium

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(C) decreases to become a constant nonzero rate at equilibrium
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Questions 29-33 refer to the following.

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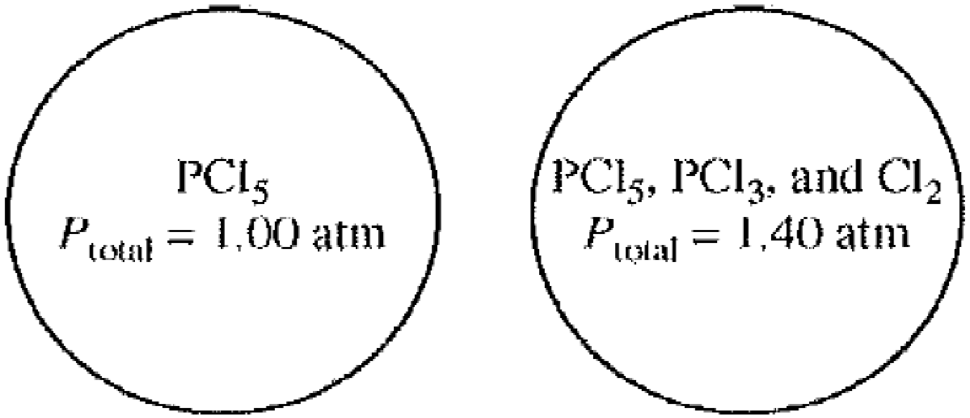

Figure 1: Initial   Figure 2: Equilibrium

32. Which of the following statements about K_p, the equilibrium constant for the reaction, is correct?

(A) $K_p > 1$

(B) $K_p < 1$

(C) $K_p = 1$

(D) It cannot be determined whether $K_p > 1$, $K_p < 1$, or $K_p = 1$ without additional information.

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Kp = $p(PCl_3)p(Cl_2)/p(PCl_5)$

Think: What would it look like if

	$PCl_5 \Leftrightarrow$	PCl_3 +	Cl_2
I	1.0	0	0
S	-x	+x	+x
E	1-x	x	x

Kp = $x^2/1$-x

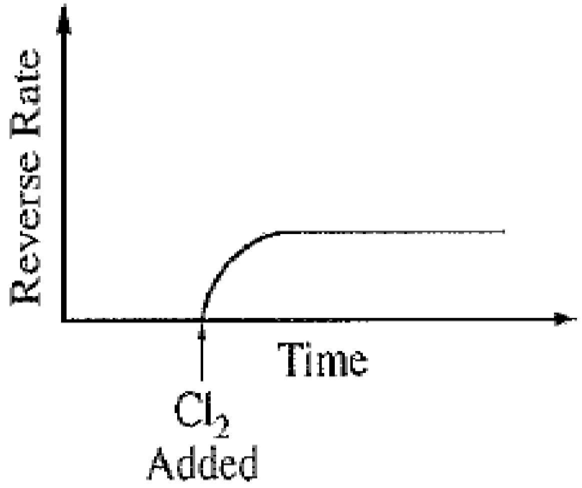
Original pressure = 1

1-1.4 = .4 difference

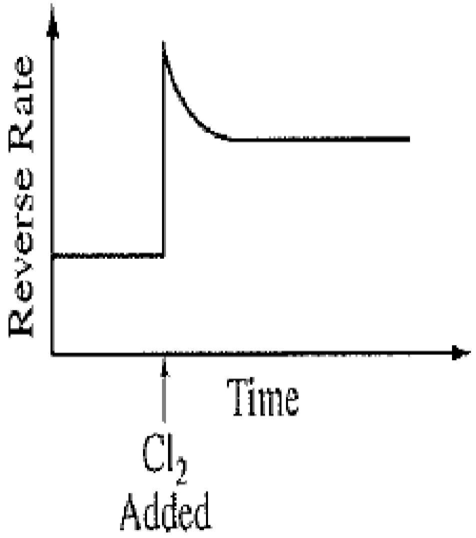
All pressures = 1.40

33. Additional $Cl_2(g)$ is injected into the system at equilibrium. Which of the following graphs best shows the rate of the reverse reaction as a function of time? (Assume that the time for injection and mixing of the additional $Cl_2(g)$ is negligible.)

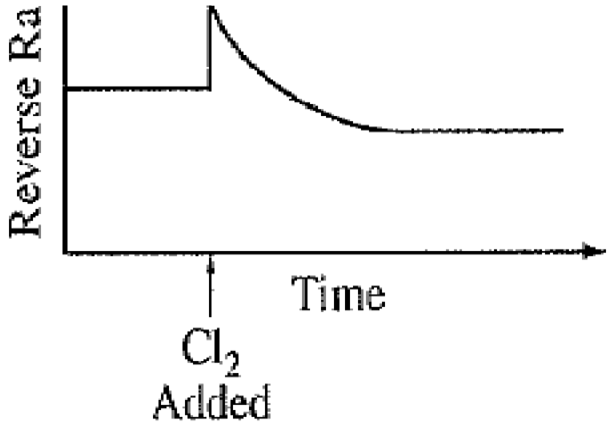
(A)



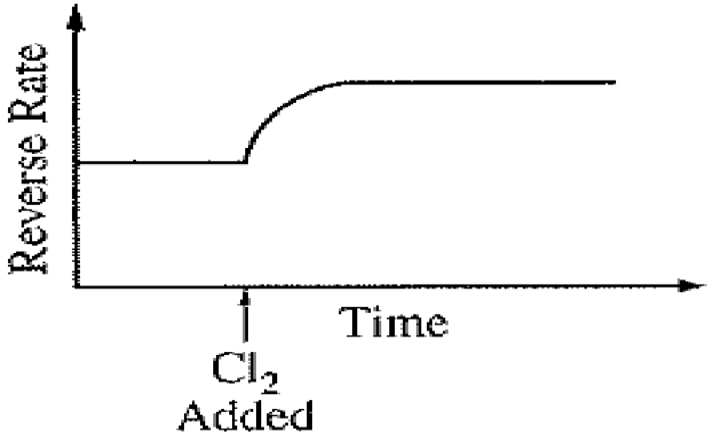
(B)



(C

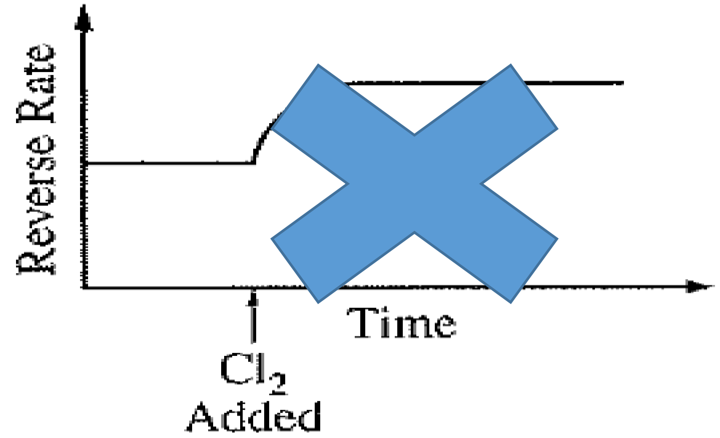


(D)

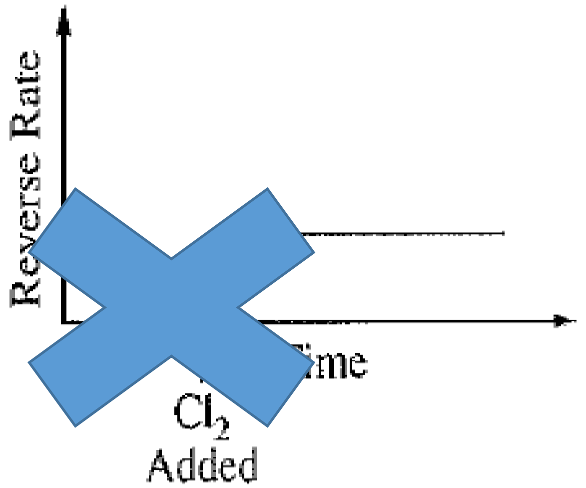


33. Additional $Cl_2(g)$ is injected into the system at equilibrium. Which of the following graphs best shows the rate of the reverse reaction as a function of time? (Assume that the time for injection and mixing of the additional $Cl_2(g)$ is negligible.)

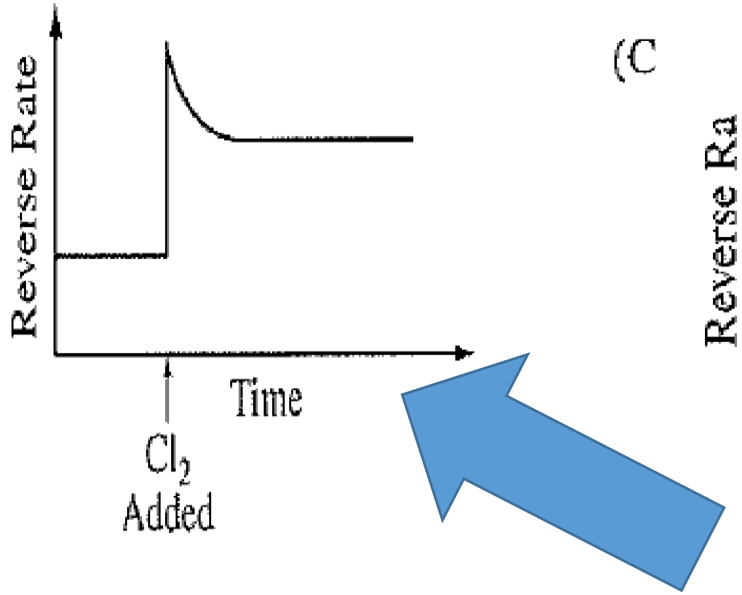
(D)



(A)



(B)



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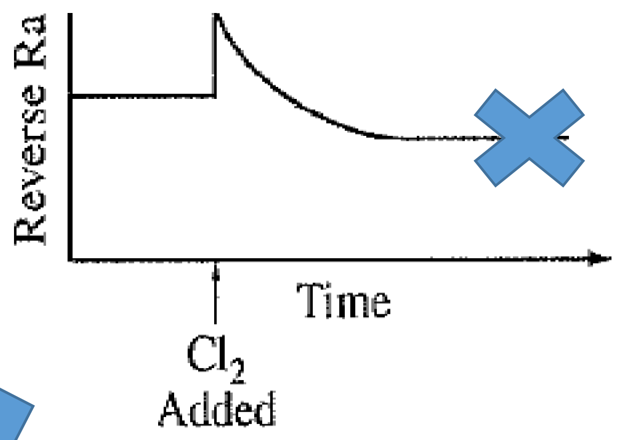

$PCl_5 \Leftrightarrow PCl_3 + Cl_2$ Reaction, will shift to reactants bit we will still have to come to a equivalent K balance. More product but more reactant as well.

Concentration (M)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

48. For which acid is the value of the acid-dissociation constant, K_a, the smallest?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) Acid 4

49. Which of the four acids listed in the table is hydrochloric acid?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) Acid 4

50. Of the following species, which has the greatest concentration in a 1.0 M solution of acid 1 at equilibrium?

(A) OH^-
(B) H_3O^+
(C) Acid 1
(D) The conjugate base of acid 1

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0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

48. For which acid is the value of the acid-dissociation constant, K_a, the smallest?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) Acid 4

For a given concentration, the weakest acid or smallest Ka will be the least acidic.

So the weakest acid here is Acid 1.

Answer is A

Concentration (*M*)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

49. Which of the four acids listed in the table is hydrochloric acid?

(A) Acid 1
(B) Acid 2 ←
(C) Acid 3
(D) Acid 4

- Again, Keep in mind a strong acid 100% ionizes. So a .01M strong acid will have a pH of 2.
- Acid 2 is the only strong acid or HCl
- Answer is B

Concentration (M)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

50. Of the following species, which has the greatest concentration in a 1.0 M solution of acid 1 at equilibrium?

(A) OH^-
(B) H_3O^+
(C) Acid 1
(D) The conjugate base of acid 1

- Keep in mind, If Acid 1 was a strong acid than the .01M would have had a pH of 2. So this acid is a weak acid and is only ionized slightly.
- Answer is C HX or acid 1

Concentration (*M*)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
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1.00	2.44	0.00	1.92	0.98

51. If equal volumes of the four acids at a concentration of 0.50 *M* are each titrated with a strong base, which will require the greatest volume of base to reach the equivalence point?

(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) All the acids will require the same volume of base to reach the equivalence point.

52. A 25 mL sample of a 1.0 *M* solution of acid 1 is mixed with 25 mL of 0.50 *M* NaOH. Which of the following best explains what happens to the pH of the mixture when a few drops of 1.0 *M* HNO_3 are added?

(A) The pH of the mixture increases sharply, because HNO_3 is a strong acid.

(B) The pH of the mixture decreases sharply, because H_3O^+ ions were added.

(C) The pH of the mixture stays about the same, because the conjugate base of acid 1 reacts with the added H_3O^+ ions.

(D) The pH of the mixture stays about the same, because the OH^- ions in the solution react with the added H_3O^+ ions.

Concentration (*M*)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
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(A) Acid 1
(B) Acid 2
(C) Acid 3
(D) All the acids will require the same volume of base to reach the equivalence point.

They all have the same volume and they have the same concentration… so they contain the same number of moles and therefore the same equivalence point. The answer is D.

Although they will not have the same pH at the end due to the acidicness of the conjugates.

Concentration (*M*)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
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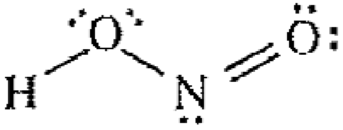
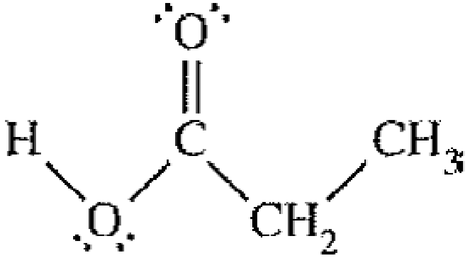
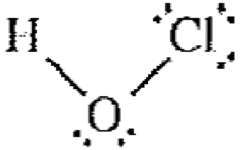
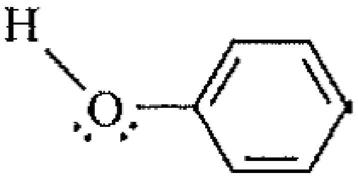
(D) The pH of the mixture stays about the same, because the OH^- ions in the solution react with the added H_3O^+ ions.

Acid 1 is a weak acid and half of it will be gone,
And half of it will get converted over to its conjugate.
This is a buffer. We will increase in pH but not that much.

Acid	Structure	K_a
HNO_2		4.0×10^{-4}
$HC_3H_5O_2$		1.3×10^{-5}
HClO		3.0×10^{-8}
HOC_6H_5		1.6×10^{-10}

55. The table above shows the values of K_a for four weak acids. Which of the following pairs of chemical species, when combined in equimolar amounts, results in a buffer with a pH closest to 7.5 ?

(A) HNO_2 and OH^-

(B) $HC_3H_5O_2$ and $C_3H_5O_2^-$

(C) HClO and ClO^-

(D) C_6H_5OH and $C_6H_5O^-$

-l0g of Ka gives buffer zone. This will be Closest to 7.

$$COCl_2(g) \rightleftarrows CO(g) + Cl_2(g)$$

60. $COCl_2(g)$ decomposes according to the equation above. When pure $COCl_2(g)$ is injected into a rigid, previously evacuated flask at 690 K, the pressure in the flask is initially 1.0 atm. After the reaction reaches equilibrium at 690 K, the total pressure in the flask is 1.2 atm. What is the value of K_p for the reaction at 690 K?

(A) 0.040
(B) 0.050
(C) 0.80
(D) 1.0

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