(Chapter 13) (13.4) **Ways of Expressing Concentration**

- **In this chapter u will face a lot of measures of concentrations , so be patient , & challenge it :D ,,, we start :**

1- **Mass Percent , ppm & ppb .** (ppm → part per million , ppb → per billion)
*** I will use Z for the mass fraction , → $\boxed{\text{Z = mass of solute/total mass}}$**

$\boxed{\text{mass \% of solute = Z * 100 \%}}$ mass% of solvent = **100 – mass% of solute**
$\boxed{\text{ppm of solute = Z * } 10^6}$ = 100 – 100Z
$\boxed{\text{ppb of solute = Z * } 10^9}$ = **(1-Z) * 100%**

* If the question gives u the **mass** of solute in **volume** of solution , & asking about ppm & ppb , then convert the unit of volume into **mL** then :
ppm = [mass(solute)/V(soln)] * 10^6 ***(soln means solution)***
ppb = [mass(solute)/V(soln)] * 10^9
look at the following example .

Example :
A solution of SO_2 in water contains 0.00023 g of SO_2 in 2 Liter solution , find ppm , ppb . → result : ppm = 0.115 g/million ppb= 115 g/billion

2- **Mole Fraction (X) .**
X = n(solute)/n(soln) , where n(soln) = n(solute) + n(solvent)

3- **Molarity (M) .**
M = n(solute)/V**(soln)** **,** (M : mol/L)
it is the only one that is $\boxed{\textbf{temperature dependent}}$

4- **Molality (m) .**
m = n(solute)/kg**(solvent)** = 1000*n(solute)/mass(solvent) (m : mol/Kg)

In the next section there is a regular way doctors told u about in order to solve the questions on it , I will not mention that way because it's too long & I don't prefer it , u have the choice , either u solve according to what I will teach u , or u go back to the slides , Book or any other source to study the regular way :) .

Converting between the different Concentration expressions

1- m → M : **M =** $\frac{d}{\frac{1}{m}+\frac{MM}{1000}}$ **,,,,,,,,,,** d : density , MM : molar mass of solute

2- M → m : **m =** $\frac{1}{\frac{d}{M}-\frac{MM}{1000}}$ **,,,,,,,,,,,** d : density , MM : of solute

3- m → mass% , ppm or ppb for solute : **Z =** $\frac{1}{1+\frac{1000}{m*MM}}$,,,,,, MM : of solute

then multiply Z by 100% , 10^6 or 10^9 to have mass% , ppm or ppb

* m → mass% for solvent , use the previous law to find Z for solute ,

then **mass% (solvent) = (1 – Z)* 100%**

4- m → X(solute) : **X =** $\frac{1}{1+\frac{1000}{m*MM.}}$ **,,,,,,,,,,,,,** MM. : molar mass of **Solvent**

5- m → X(solvent) , use the previous law to find X(solute) then :

X(solvent)= 1 - X(solute)

6- mass% solute → M : **M = dZ*1000/MM** ,,,,,,,,, MM is for solute .

* Z = mass%/100 . * If u want M of pure liquid → **M = d*1000/MM**$_{\textbf{liquid}}$

7- mass% solute → m : **m =** $\frac{Z}{1-Z} * \frac{1000}{MM}$ **,,,,,,,,,,,,,,,** MM is for solute

* $\frac{Z}{1-Z}$ **= mass (solute)/mass (solvent)** so if u know the masses, use them

8- X → m : **m =** $\frac{X}{1-X} * \frac{1000}{MM.}$ **,,,,,,,,,,,,,,,,,,,** MM. is for **Solvent**

9- X → mass% : **Z =** $\frac{1}{1+\frac{(1-X)MM.}{X*MM}}$ **,,,,,,,,,,,** then multiply Z by 100%

MM. is for solvent , MM of solute in this & next equations

10- mass% → X : **X =** $\frac{1}{1+\frac{(1-Z)MM}{Z*MM.}}$ **,,,,,,,,,,,** * Z = mass%/100

- **The units of density u must use in these laws are : g/mL or g/cm^3 or Kg/L**

- To save these equations better , take these hints :

- **the first 2 equations (#1 & #2)** :

  d & M are always together so when we want M → M = $\frac{\mathbf{d}}{\mathbf{etc}}$,

  & when we want m → m = $\frac{\mathbf{1}}{\frac{\mathbf{d}}{\mathbf{M}}\mathbf{...etc}}$.

  Regarding the sign in the equation , after $\frac{\mathbf{d}}{\mathbf{M}}$ we put minus , while after $\frac{\mathbf{1}}{\mathbf{m}}$ we put plus , because the first one has two variables so we subtract , but the second one has 1 variable , so we add . :P
- **Equations #3 & #4** : they are exactly the same , but always with X → the MM is for the solvent , while <u>all other cases , the MM is for the solute</u> .
- **Equation #6** , save this mnemonic : M = دز الف بالمَيّه . :P
- **Equations #7 & #8 ,** I think they are somewhat easy to save but notice that with X → MM is for solvent (in #8) as we said above **.**
- **Equations #9 & #10 ,** as we said , with X , MM is for solvent , so in #9 the MM which is after (1-X) directly is for solvent & the other is for solute , while in #10 , MM after (1-Z) directly is for solute , & the other is for solvent . **(so here we look to (1-X & 1-Z) to determine the MM , not to X/Z themselves) .**

- These equations are 100% correct & perfect , I derived them , they solve the complex questions on this section in only one step (put the things given in the question in the needed equation & solve by ur calculator) .

  The importance of them is that in the exam u will waste too much time understanding & connecting information then u will waste another time using different basic laws in multi-steps to solve & the exam time is limited Another point is that the more steps u take the more chances for errors in each step , also it becomes harder to check after u complete the exam .
  So these laws are direct easy & quick ways to solve & check .

  If u decide to use them , **save them by heart** , because any mistake in writing or remembering them → completely false answers .

Questions on the Concentration Expressions

- A solution is made by dissolving 13.5 g of glucose in 0.1 Kg of water .
  find the mass percent of glucose .
  Answer : mass(soln) = mass glucose + mass water(in grams)
  = 13.5 + (0.1 *1000) =113.5 g
  then , Z = mass solute/mass(soln) = 13.5 / 113.5 = 0.119
  so mass % = Z *100% = 11.9 %

- If 5.4 μg of Zn^{+2} is dissolved in 2.5 g water . find ppm for Zn^{+2} .
  Answer : mass (soln) ~ mass of water alone = 2.5 g
  Z = mass solute/mass soln = 5.4 * 10^{-6} / 2.5 = 2.16 * 10^{-6}
  → ppm = Z * 10^{6} = 2.16

- If 4.35 g of glucose (MM = 180) is dissolved in 25 mL water at 25 °C , find glucose Molality (m) if u know that d(water) = 1 g/mL .
  Answer : we must find both moles of glucose & mass of water .
  we use MM to change mass of glucose to moles : n = 4.35/180 =0.024
  we use density to change the volume of water to mass :
  mass(water) = d*V = 1 g/mL * 25 mL = **25 g**
  finally , use Molality basic Law in the beginning ,,,,,,,, result = 0.96 m .

- An aqueous solution contains 36 % HCl by mass , calculate the mole fraction for HCl . (MM for HCl = 36.5)
  Answer : "by mass" means mass fraction → Z = 0.36 ,,,, use equation #10
  the result = 0.217 (the solvent is water , MM = 18)

- Calculate the Molality for HCl in the previous Qs .
  (use equation #7 , the answer = 15.4)

- A solution with density of 0.876 g/mL contains 5 g of C_7H_8 & 225 g of benzene. Find M of C_7H_8 . (MM of benzene = 92**)**
  Answer : the solvent here is benzene & **mass(soln) = 5 + 225** = 230 g
  → Z = 5/230 = 0.0217 ,,,,, then use equation #6 , the result = 0.207 M

- A solution containing equal masses of glycerol & water , has a density of 1.1g/mL , Calculate (m , X & M) for glycerol . (M.M for glycerol = 92) .
  Answer : equal masses → Z = 0.5 → use #8 for m , #11 for X , & #7 for M

- If a density of 2.73 m aqueous solution of CH_3OH equals 0.976 g/mL , (MM of CH_3OH =32) , then :
  1- find M . →→ (**m=2.73** ,,, use #2 ,,, the answer = 2.45)
  2- mass% of CH_3OH . → (use #3 ,,, the result = 8 %)
  3- mass% of water . → (use the * of #3 ,,, result = 92 %)
  4- ppm for CH_3OH . → (use #3 ,,, answer = 80000) .
  5- Calculate X for solvent . → (use #5 ,,, answer = 0.953)

- A sulfuric acid solution containing 571.6 g of H_2SO_4 per liter of solution has a density of 1.329 g/mL . Calculate the mass percent .
  Answer : when you have such questions where they give u the concentration in **mass per volume** & ask about a **fraction** like X , Z or mass % , then u can suppose that u have 1 unit volume of the solution , then solve . (**because any volume u suppose will be cancelled while solving these questions , so it will not affect the end result**)
  Now let's suppose that we have 1 liter solution :
  then we have 571.6 g H_2SO_4 (because in each liter we have that number)
  After that we just need the mass of solution (to find Z then find mass%) .
  we find it using the density :
  mass (soln) = d*V = 1.329 g/mL * **1000 mL** = 1329 g (notice 1000 mL= 1L)
  Now we find Z = 571.6/1329 = 0.43 → mass% = 43%

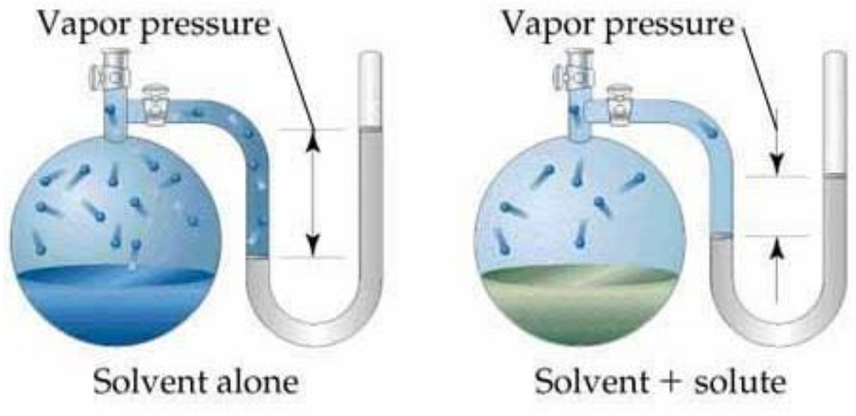
- Calculate the molar Concentration of pure water at 25 ^{o}C , given that density of water = 1 g/mL .
  Answer : use the * of #6 (with pure liquids)
  → M = d*1000/MM = 1*1000/18 = 55.55556 mol/L

(13.5) **Colligative Properties**

- They are physical properties that depend on the number of particles in solution but not on the kind of these particles .

- They are :
  1- lowering the vapor pressure . 2- Osmotic pressure .
  3- Boiling Point elevation . 4- Freezing point depression .

Lowering the vapor pressure



As u see in the picture, when the solvent is pure, the vapor is at the max → the pressure of this vapor is high, but when a nonvolatile solutes is mixed with the solvent, the vapor is decreased → the vapor pressure is decreased .

We refer to the Vapor pressure above pure solvents → P^o ,
while the one above the solution → P

As described, $P < P^o$, the Law which connects these pressures is **Raoult's Law** :

$$\boxed{P = X(\text{solvent}) * P^o}$$

$$\boxed{\text{Vapor Pressure Lowering } (\Delta P) = P^o - P}$$

$$\boxed{\Delta P = X(\text{solute}) * P^o}$$

$X_{\text{solvent}} = n_{\text{solvent}} / (n_{\text{solvent}} + n_{\text{solute}})$ but if the solute is a strong electrolyte :
$X_{\text{solvent}} = n_{\text{solvent}}/(n_{\text{solvent}} + i*n_{\text{solute}})$ where i = # of ions in the formula

Examples :

- If u know that (P^o for water = 42.18 torr) **,** Calculate the vapor pressure & the vapor pressure lowering for a solution made by dissolving :
  1- 30 g of urea (MM=60) in 180 g water . 2- 60 g of urea in 180 g water .
  Answer :

1- n for water = mass/MM = 180/18 = 10 mol

n for urea = 30/60 = 0.5 mol → X_{water} = 10/(10 + 0.5) = 0.95

→P = X(solvent)*P° = 0.95*42.18 = 40.07 torr

→ΔP = P° - P = 42.18 – 40.07 = 2.11 torr Or ΔP = X(solute) * P°

2- n for water = 10 mol ,, n for urea = 60/60 = 1 mol

X_{water} = 10/(10 + 1) = 0.91

→P = X*P° = 0.91*42.18 = 38.35 torr → ΔP = 42.18 - 38.35 = 3.83 torr

**** as u see , the more particles (moles) of Urea , the more lowering in vapor pressure .**

- If u know that (P° for water = 42.18 torr) , Calculate the vapor pressure & the vapor pressure lowering for a solution made by dissolving :

  1- 60 g of Urea (MM=60) in 180g water . 2- 58.5g of NaCl in 180g water

  Answer :

  1- From the previous Qs , P = 38.35 torr → ΔP = 3.83 torr

  2- n for water = 10 mol ,,, n for NaCl = mass / MM = 58.5/58.5 = 1 mol

  X_{water} = 10/(10 + **i***1) = 10/(10+ 2*1) = 10/12 = 0.83

  →P = X*P° = 0.83*42.18 = 35 torr → ΔP = 42.18 – 35 = 7.18 torr

  ***** as u see , the more particles in NaCl (electrolyte) lower the vapor pressure more than Urea(molecular compound) . even that they have the same number of moles & the same mass , because NaCl gives 2 particles (ions) but Urea give only one per each molecule in water.**

- **The More Particles amount (moles , molality , molarity) in a solution → The less Vapor pressure & The more ΔP .**

- Rank the following according to vapor pressure over their aqueous solutions :

  a) 0.1 m $C_6H_{12}O_6$. b) 0.1 m $FeCl_3$.

  c) 0.1 m $NaCl$. d) 0.1 m Na_2SO_4 .

  Answer :

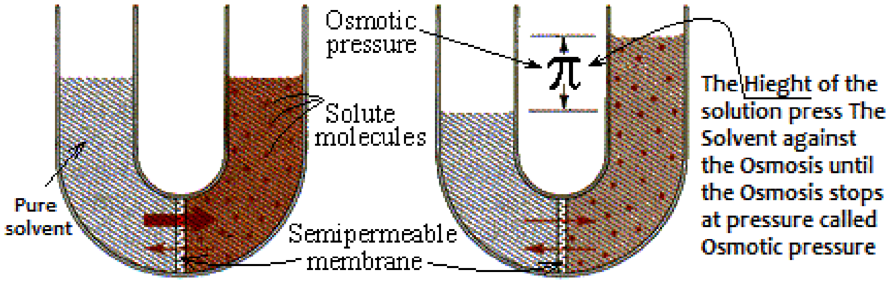
  (multiply the molality of each with **i** to know **the molality of particles**)

  a) 0.1 b) 0.1*4 = 0.4 c) 0.1* 2= 0.2 d) 0.1* 3= 0.3

  the more particles the less P → b<d<c<a

  → $C_6H_{12}O_6 > NaCl > Na_2SO_4 > FeCl_3$

Osmotic Pressure



The Hieght of the solution press The Solvent against the Osmosis until the Osmosis stops at pressure called Osmotic pressure

- **Osmosis** : the net movement of solvent molecules through a semi permeable membrane into a higher solute concentration, to equalize the solute concentrations on the two sides .

  *** IF we have a pure solvent (concentration of solute = 0) in one side & a solution in the other side, the osmosis can never stop by equalizing the two sides , because the solution concentration can never reach 0 , in this case when the column of solution becomes high enough ,it exerts a pressure called **Osmotic Pressure** opposite to the force of osmosis , leading to stop the osmosis (the movement) .

- **Osmotic Pressure (π) of a solution :** it's the pressure at which the osmosis stops if this solution is put in one side of a semi permeable membrane , & a pure solvent at the other side **.**

  The more osmotic pressure , the higher the solution column , look at the picture previously .

- $\boxed{\pi V = RnT \quad \leftrightarrow \quad \pi = MRT}$ (M:molarity)

- For strong electrolytes : $\boxed{\pi V = i^{*}RnT \quad \leftrightarrow \quad \pi = i^{*}MRT}$

If u recall , this is very similar to the Ideal gas law ,,, except that the Ideal gas law deals with pressures of <u>**gases**</u> , while this law deals with osmotic pressures of <u>**solutions**</u> .

- **Examples :**

- what is the osmotic pressure at 20 °C of 0.002 M sucrose solution .

  Answer : π = MRT = 0.002 * 0.0821 * 293 = 0.048 atm

- If 5.85 g of NaCl dissolved in water & gave a solution with osmotic pressure of 2 atm at 25 ^oC .
  what is the solution volume ??

  Answer : (i = 2 , n=mass/MM=5.85/58.5=0.1) → **πV = i*RnT**

  → **V = i*RnT/π** = 2*0.0821*0.1*(25+273)/2 = 2.45 L

- If u focus in the law → the more (M)or (i), the more osmotic pressure so **: The More Particles amount (moles , Molarity or molality) , the more Osmotic Pressure .**

- Rank the following according to increasing Osmotic Pressures:
  a) 0.2 m **$KClO_4$** . → **i** = 2 → m(particles) = 2*0.2 = 0.4
  b) 0.1 m **Al_2O_3** . → **i =** 5 → m(particles) = 5*0.1 = 0.5
  c) 0.15 m **CaI_2** . → **i =** 3 → m(particles) = 3*0.15 = 0.45
  d) 0.15 m **$AlCl_3$.** → **i =** 4 → m(particles) = 4*0.15 **=** 0.6
  so **$AlCl_3$ > Al_2O_3 > CaI_2 > $KClO_4$**

- The most useful Application of Osmotic pressure Law is to **determine the Huge molar masses** of some compounds : $\boxed{\mathbf{M.M = R*mass*T/\pi V}}$
  (remember , in Ideal gas law : M.M = R*mass*T/PV = RdT/P ,,, very similar)

  Example :

- If 20 mg of a protein dissolved in water & gave 25 mL of solution has an osmotic pressure of 0.56 torr at 25 ^oC . what is the molar mass of this protein ?

  Answer : M.M = R*mass*T/πV

  = 0.0821* (20*10^{-3}) * (298) /[(.56/760)*(25*10^{-3})] = 26.56 **Kg**/mol

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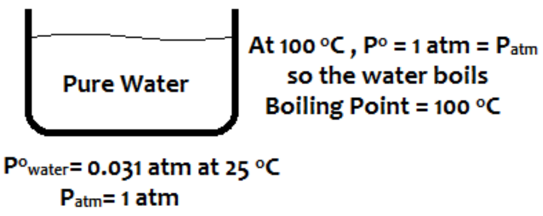
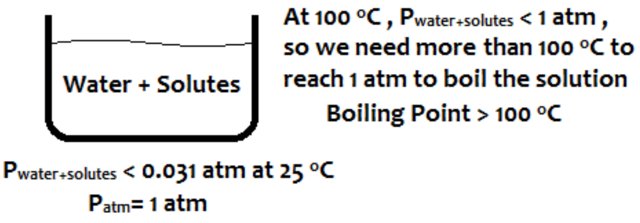
Boiling Point Elevation





- Boiling Point : the temperature at which the vapor pressure of a liquid equals to the atmospheric pressure , which make the liquid boils .

- One way to increase the vapor pressure of a liquid is to increase its temperature , so we can let the vapor pressure reach the atmospheric pressure & the boiling occurs by increasing the temperature .

- Now , If we decrease the initial vapor pressure (by mixing solutes with the liquid) , we need more temperature than the pure liquid need , to let the vapor pressure reach the atmospheric pressure , which means the temperature at which the vapor pressure is equal to atmospheric pressure is more than that of pure liquid → the Boiling Point increases .

$$\boxed{\Delta T_b = K_b * m}$$

For Strong Electrolytes : $\boxed{\Delta T_b = i * K_b * m}$

$$\boxed{\Delta T_b = T_b(\text{soln}) - T_b(\text{pure solvent})}$$

T_b : boiling point (temperature of boiling) .
ΔT_b : boiling point elevation (T_b difference between pure liquid & its soln)
ΔT_b is always positive , because T_b(soln) > T_b(solvent)
K_b : molal boiling-point-elevation constant , it is **<u>Solvent Dependent</u>** means that each solvent has its K_b .
it's units : <u>^{o}C/molal</u> or <u>K/molal</u> , & <u>^{o}C.kg/mol</u> or <u>K.kg/mol</u>

- **The More Particles (moles , m , M) the Higher Boiling Point & Boiling Point Elevation** .

Now let's have Examples :

- Calculate the Boiling Point of a 25 mass % solution of ethylene glycol (nonvolatile & nonelectrolyte) in water . (MM for ethylene glycol = 62.1 g/mol),($K_{b \text{ for water}}$ = 0.51 ^{o}C/m)
Answer : we use equation #6 to find molality from mass % :
m = Z/(1-Z) * 1000/MM = 0.25/0.75 * 1000/62.1 = 5.37 m
now $\mathbf{\Delta T_b = K_b * m =}$ 0.51 *5.37 = 2.7 ^{o}C
$\Delta T_b = T_b(\text{soln}) - T_b(\text{solvent}) \rightarrow T_b(\text{soln}) = \Delta T_b + T_b(\text{solvent})$
= 2.7 + <u>100</u> = 102.7 ^{o}C . (notice that T_b for pure water = 100 ^{o}C)

- Rank the following according to their Boiling Point Elevation :

  1- 0.1 m NaI . → i = 2 → m(particles) = 0.2 m
  2- 0.005 m Na_3PO_4 . → i = 4 → m(particles) = 0.02 m
  3- 0.05 m FeI_2 . → i = 3 → m(particles) = 0.15 m
  4- 0.2 m $KClO_4$. → i = 2 → m(particles) = 0.4 m
  Answer : →→ **$KClO_4 > NaI > FeI_2 > Na_3PO_4$**

Freezing Point depression

- Freezing point : the temperature at which the liquids start turning into solids by crystallization .

- In order for a liquid to freeze, its components need to get closer and closer until they pack enough to form crystals of solid. If we dissolve particles ,it becomes difficult for the liquid to "pack" into its crystals . To overcome this difficulty , you have to lower the temperature even more than usual (lower than the freezing point of the pure solvent) to finally achieve the "packing" of the particles needed in Crystals of solid . This means that :

  The Freezing Point decreased for the solutions comparing with the pure solvent , & the difference between the two freezing points (solution & solvent) = **freezing point depression** .

$$\boxed{\Delta T_f = K_f * m}$$

For Strong Electrolytes : → $\boxed{\Delta T_f = i * K_f * m}$

$$\boxed{\Delta T_f = T_f(solvent) - T_f(soln)}$$

ΔT_f is always + , because $T_f(solvent) > T_f(soln)$

T_f : freezing point , ΔT_f : freezing point depression , K_f : the same as K_b

- **The More Particles (moles,m ,M) the Lower Freezing Point & higher Freezing Point Depression**
- For All Colligative Properties :

  The More Particles Concentration →

  the more (ΔP) , (ΔT_f) , (ΔT_b) , (T_b) & (π) BUT the less (P) & (T_f) .

Example :

- Calculate the freezing point of solution made by dissolving 0.24 mol of a gas in 58 g benzene . giving that T_f (benzene) = 5.5 ^oC , K_f (benzene) = 5.12 $^oC/m$

  Answer :

  m = 1000n/mass(solvent) = 1000*0.24/58 = 4.14 m

  $\Delta T_f = K_f * m$ = 5.12 * 4.14 = 21.2 ^oC , $\Delta T_f = T_f(benzene) – T_f(soln)$

  →→→ result : $T_f(soln) = -15.7$ ^oC

- To determine the M.M for compounds after we are given info about boiling points or freezing points , firstly find the molality (m) = $\Delta T/K$, then :

  MM(solute) = mass(solute)/mass(solvent) * 1000/m

  (this is the same of equation #7 in the beginning , with changing positions of MM & m only)

  Examples :

  - A solution made by dissolving 0.85 g of unknown organic compound in 100 g of benzene has a freezing point of 5.16 ^oC . Calculate MM for the compound .(use the constants of benzene in the previous Example).

    Answer :

    $\Delta T_f = T_f(benzene) – T_f(soln) = 0.34$ ^oC → m = $\Delta T_f/K_f$ = 0.34/5.12= 0.0664 m

    MM(solute) = mass(solute)/mass(solvent) * 1000/m →→→ = 128 g/mol

  - Rank the following according to their freezing points :

    1) 0.1 m **Al_2O_3** . → **i =** 5 → m(particles) = 5*0.1 = 0.5
    2) 0.2 m **$KClO_4$** . → **i** = 2 → m(particles) = 2*0.2 = 0.4
    3) 0.15 m **$AlCl_3$.** → **i =** 4 → m(particles) = 4*0.15 = 0.6
    4) 0.15 m **CaI_2** . → **i =** 3 → m(particles) = 3*0.15 = 0.45

    so : **$AlCl_3 < Al_2O_3 < CaI_2 < KClO_4$**

End Of Chapter 13

Ch.14 **Chemical kinetics**

(14.1) **Factors that Affect Reaction Rates**

The following factors increase the rate of reaction :

1- the Temperature . 2- the Concentration of reactants .

3- The Surface of contact . 4- the presence of Catalysts .

(14.2) **Reaction Rates**

- **The rate of reactant's disappearance** : The Changing in reactants Concentration per unit of time .

- **The rate of product's appearance** : The Changing in products Concentration per unit of time .

- **The rate of reaction** : the Changing of concentration per unit of time **for every 1 mol of any reactant or product** , which means that the rate of reaction is the rate of 1 mol of its reactants or products .

Explanation

Suppose u have this reaction : $A \rightarrow B$, then A is the reactant , B is the product .

Now because the coefficients are equal to 1 , then :

Rate of the reaction = Rate of disappearance of A = Rate of appearance of B

but If we have this reaction : $2A \rightarrow 3B$, then the coefficients aren't equal to 1 , so the rate of reaction is different from the rate of appearance or disappearance : (rxn : reaction)

Rate of rxn = 1/2*(rate of disappearance of A)= 1/3*(rate of appearance of B)

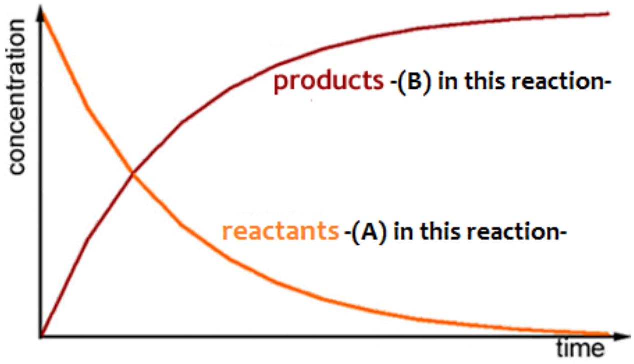
we divide by the coefficients to have the rate of 1 mol of reactants/products which is equal to the reaction rate .

- We refer to the concentration by this symbol **[ ]** & the changing in concentration by **Δ[ ]**
  so in the previous example :
  rate of disappearance of A = $-\Delta[A]/\Delta t$
  rate of appearance of B = $\Delta[B]/\Delta t$
  & the **Reaction Rate =** $1/2 * (-\Delta[A]/\Delta t) = 1/3 * (\Delta[B]/\Delta t)$

- **$\Delta[\ \ ] = [\ \ ]_t - [\ \ ]_o$**

  $[\ \ ]_t$: the concentration after a time, $[\ \ ]_o$: the initial concentration .

  Δ[reactant] will be negative always , because $[\ \ ]_t < [\ \ ]_o$ always , so to have a positive value of rate (rate=speed , & we never have a negative speed , it's a positive value always) , we put the minus sign (**-**) before the rate of disappearance of reactants .



So the Law of Reaction Rate for this reaction : (a A + b B → c C)

-where a , b & c are the coefficients- **is :**

Rxn Rate = 1/a * rate of disappearance of A = 1/b *rate of disappearance of B
= 1/c * rate of appearance of C

$$\boxed{\textbf{Rxn Rate} = -1/a * \Delta[A]/\Delta t = -1/b * \Delta[B]/\Delta t = 1/c * \Delta[C]/\Delta t}$$

This rate law refers to what we call : <u>the average rate</u> along a time interval .

- **Examples** :

- for the reaction : (A → B) , if the initial concentration of A was 1 M & after 20 seconds became 0.5 M , calculate the rate of disappearance of A .
  Answer : rate of A = $-\Delta[A]/\Delta t = -(0.5 - 1)/(20-0) = 0.5/20 = 0.025$ M/s

- consider this reaction : ($2\ H_2 + O_2 \rightarrow 2\ H_2O$) , If the initial concentration of H_2O was 3 M , & the rate of appearance of H_2O is 0.05 M/s .
  Calculate the concentration of H_2O after 10 seconds **.**
  Answer : rate of $H_2O = \Delta[H_2O]/\Delta t \rightarrow 0.05 = ([H_2O]_t - 3)/10 \rightarrow$
  $0.5 = [H_2O]_t - 3 \rightarrow [H_2O]_t = 3.5$ M

- How is the rate of Ozone disappearance related to the rate of oxygen appearance , in the reaction : $2\ O_3 \rightarrow 3\ O_2$? .
  hint (use the previous rate law to know the relationship between them)
  Answer : 1/2 * Rate of O_3 disappearance = 1/3 * Rate of O_2 appearance
  this relationship is always true at any time .

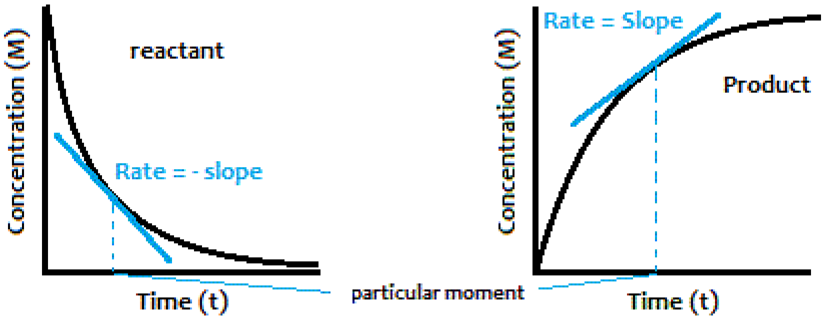
- In the previous example , If the rate of O_2 appearance = $6 * 10^{-5}$ M/s at particular moment , Calculate the rate of O_3 disappearance at the same moment .
  Answer : using the previous relationship :
  1/2 * Rate of O_3 = $1/3 * 6 * 10^{-5}$ → Rate of O_3 = $4*10^{-5}$ M/s

- The Decomposition of N_2O_5 proceeds according to : ($2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$)
  If the rate of decomposition of N_2O_5 at a particular instant = $4.2 * 10^{-7}$ M/s , what is the rate of appearance of NO_2 ???
  Answer : from the law of reaction rate :
  1/4 rate of appearance of NO_2 = 1/2 rate of disappearance of N_2O_5
  → rate of NO_2 = 2* rate of N_2O_5 → rate of NO_2 = $2*4.2*10^{-7}$ = $8.4*10^{-7}$ M/s

- The rate of any reaction decreases with time , because the initial concentrations decreases .

Instantaneous Rate

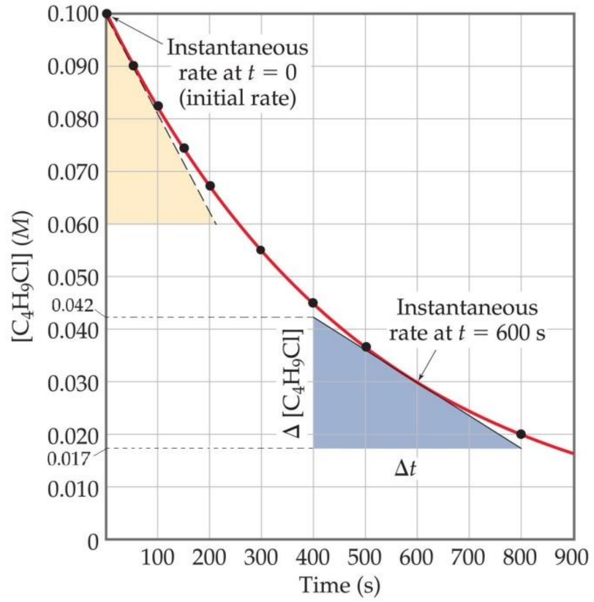
- Instantaneous Rate : the rate at a particular moment .
- It is determined from the slope (ميل) of the tangent (مماس) at that moment on the average rate curve , but because the rate is a positive value , we multiply the slope with (-) if it was negative .
  as shown in the picture :



Example :

$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$

If u have the following figure for C_4H_9Cl concentration/time :



1- Calculate the instantaneous rate of disappearing at t = 600 s .

Answer :

rate = - slope = - $\Delta[C_4H_9Cl] / \Delta t$

= - (0.017-0.042)/(800-400)

= $0.63 * 10^{-4}$ M/s

2- Calculate the instantaneous rate of disappearing at t = 0 s .

Answer :

rate = - (0.06 – 0.1)/(200 – 0)

= $2*10^{-4}$ M/s

* notice the decrease in rate at 600 s comparing to the initial value at 0 s , this is because the reactants concentration is decreased .

(14.3) **The Rate Law (the effect of concentrations on the rate)**

- as we said previously , the rate of any reaction depends on the concentrations of the reactants , so if we have a reaction with 1 reactant (Example : A → B) then : rxn Rate $\propto$ [A]

  → rxn **Rate = K * $[A]^x$** = $\Delta[A]/\Delta t$

  K : the rate Constant (temperature dependent) , larger K → faster rxn .

  x : the order of reaction with respect to A .

1- If x = 1 , this means : the rate Change by the same change of [A]
2- If x = 2 , this means : the rate Change by 2 of the change of [A]
3- If x = 0 , this means : the rate isn't affected by the changing of [A]
4- If x = -1 , this means : the rate oppositely change by the same change of [A]
5- If x = -2 , this means : the rate oppositely change by 2 of the Change of [A]

What does that mean ??

for x = 1 →

if we increase [A] to the double , the rxn rate will be doubled .

if we increase [A] 3 times , the rxn rate will increase 3 times .

for x = 2 →

if we increase [A] to the double , the rxn rate will increase 4 times (2*2) .

if we increase [A] 3 times , the rxn rate will increase 9 times (3*3)

for x = 0 → if we increase or decrease [A] to any value ,nothing changes in rate

for x = -1 →

if we increase [A] to the double , the rxn rate decrease to the half .

if we increase [A] 3 times , the rxn rate decrease 3 times .

for x = -2 →

if we increase [A] to the double , the rxn rate will decrease 4 times.

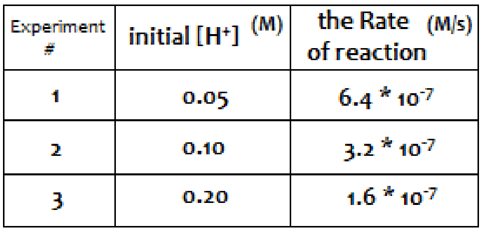
if we increase [A] 3 times , the rxn rate will decrease 9 times .

if [A] decreased rather than increased, just reflect the previous statements .

Examples

- If we have (A → 2 B) , & we made 2 experiments . In the first one , we prepared 10 M [A] & the rate was 2 M/s , in the second we prepared 20 M [A] & the rate was 4 M/s , what is the order of reaction with respect to A ?
  Answer : according to what we said before : x = 1 .

- In the same previous example , If the second experiment was : 20 M [A] but the rate was 0.5 M/s , what is the order of reaction with respect to A ?
  Answer : the rate decreases 4 times when [A] increases to the double , so
  x = -2



Experiment #	initial $[H^+]$ (M)	the Rate of reaction (M/s)
1	0.05	$6.4 * 10^{-7}$
2	0.10	$3.2 * 10^{-7}$
3	0.20	$1.6 * 10^{-7}$

- $2\,H^+ + 2\,e^- \rightarrow H_2$
  what is the order of reaction with respect to H^+ according to the data in the table ?
  Answer :
  the rate decreases to half when $[H^+]$ doubles , so the order of H^+ = -1 .

How to find x in basic way ?

we take any two experiments from the table , then we write the law for each one , then divide the two equations on each other , then we take the log & find x , let's take the previous example & solve it in this way :

I will take experiments 1 & 2 :

The rate law for experiment 1 : Rate = $K*[A]^x$ → $\mathbf{6.4 * 10^{-7} = K*(0.05)^x}$

The rate law for experiment 2 : Rate = $K*[A]^x$ → $\mathbf{3.2 * 10^{-7} = K*(0.10)^x}$

now divide the two equations → $\frac{6.4 * 10{\wedge}{-7}}{3.2 * 10{\wedge}{-7}} = \frac{K*(0.05){\wedge}x}{K*(0.10){\wedge}x}$, K is cancelled :

→ $2 = (\frac{(0.05)}{(0.10)})^x$ → $2 = 0.5^x$, take the log in each side → log 2 = x*log 0.5

→→ x = -1 .

if [A] increases or decreases & the value of rate increases or decreases in a manner not one of the previous five situations (meaning that when the quick method of solving isn't applicable) , we use this basic way & find x .

- **Now If we have multi reactants (A + B → C) , the rate law is :**

Rate = K $[A]^X$ $[B]^Y$

if it was (A + B + C → D) → **Rate = K $[A]^X$ $[B]^Y$ $[C]^Z$**

x : the order of reaction with respect to A .

y : the order of rxn with respect to B . z : the order with respect to C .

for (A+B →C) , the overall order of reaction = (x + y)

but for (A+B+C →D) the overall order = (x + y + z)

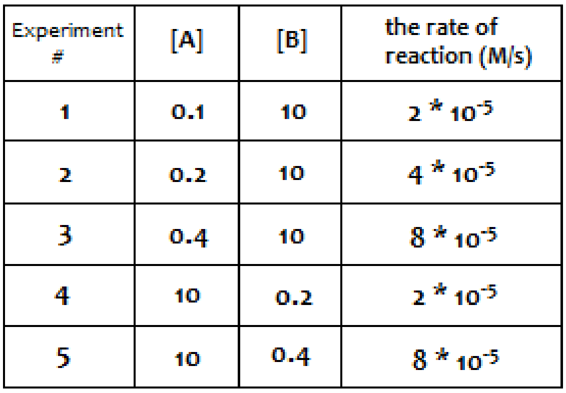
- the unit of K represents the overall order of reaction , as the following :

$\boxed{s^{-1} \rightarrow 1^{st}\text{ order}}$. $\boxed{s^{-1} M^{-1} \rightarrow 2^{nd}\text{ order}}$. $\boxed{s^{-1} M^{-2} \rightarrow 3^{rd}\text{ order}}$.

$\boxed{s^{-1} M^{-3} \rightarrow 4^{th}\text{ order}}$. $\boxed{M/s \rightarrow \text{Zero Order}}$.

- **Examples :**

- Consider the following kinetic data for the reaction : (A + B → P)
  - **write the reaction rate law .**



Experiment #	[A]	[B]	the rate of reaction (M/s)
1	0.1	10	$2 * 10^{-5}$
2	0.2	10	$4 * 10^{-5}$
3	0.4	10	$8 * 10^{-5}$
4	10	0.2	$2 * 10^{-5}$
5	10	0.4	$8 * 10^{-5}$

Answer : the law :

Rate = K $[A]^X$ $[B]^Y$

but we must find x , y .

To find them , u should study the effect of [A] on the rate in constant [B] & the effect of [B] on rate in constant [A] , like the following :

study experiments (1 & 2) to find x (because [B] is constant) , as u can see **x = 1** & by studying (4 & 5) (constant [A]) → we conclude that **y = 2** , because when [B] increases to the double , the rate increases 4 times .

So **Rate = K [A][B]^2 .**

- **What is the overall order of the previous reaction ??? → 3**
- **Find K for the previous example .**
  take one experiment , for example #1 → K = rate/[A][B]^2 →
  K = $2*10^{-5}/(0.1*10^2) = 2*10^{-6}$ s^{-1} M^{-2} (we use this unit because the reaction is 3rd order)

- Consider the following kinetic data for the reaction: ($2NO + 2H_2 \rightarrow N_2 + 2H_2O$) **Find the order of reaction with respect to H_2 & NO.**
  By studying experiments (1 & 2)→ x = 1
  By studying experiments (1 & 3)→ y = 2

Experiment #	[H_2]	[NO]	the rate of reaction (M/s)
1	0.01	0.025	$2.4 * 10^{-6}$
2	0.005	0.025	$1.2 * 10^{-6}$
3	0.010	0.0125	$6.0 * 10^{-6}$

- Consider the following rate data for the reaction (A + B → C)

Find : 1- the rate law .
2- the rate Constant .
3- the rate when [A] = 0.050 M

Experiment #	[A]	[B]	the rate of reaction (M/s)
1	0.100	0.100	$4.0 * 10^{-6}$
2	0.100	0.200	$4.0 * 10^{-6}$
3	0.200	0.100	$16.0 * 10^{-6}$

Answer :

1- by studying (1 & 2) → y = 0
by studying (1 & 3) → x = 2
→ rate = $K[A]^2[B]^0 = K [A]^2$

2- take experiment 1 → K=rate/$[A]^2$ = $4*10^{-6}$**/**$(0.1)^2$ →→ K = $4 *10^{-4}$ s^{-1} M^{-1}
(the unit is this , because the overall order = 2)

3- the rate law = $4 * 10^{-4} * [A]^2$,,,[A]=0.05,,, →→→ rate = $1 * 10^{-6}$ M/s

How to find x & y in a basic way ?

we take 2 experiments in which y is constant to find x , & another 2 experiments in which x is constant to find y :

in the previous example : we take experiments (1 & 2) to find y :
in experiment 1 : Rate = $K [A]^X[B]^Y \rightarrow 4 * 10^{-6} = K (0.1)^X(0.1)^Y$
in experiment 2 : Rate = $K [A]^X[B]^Y \rightarrow 4 * 10^{-6} = K (0.1)^X(0.2)^Y$
divide the two equations & cancel K & $[0.1]^X \rightarrow 1 = (\frac{(0.1)}{(0.2)})^Y \rightarrow 1 = 0.5^Y$
take log → log 1 = y*log 0.5 → y = 0
we take experiments (1 & 3) to find x ,,, & we do the same steps .

we use this basic way to find x , y when the quick method is not applicable .

(14.4) **The Change of Concentration with time**

First order reactions

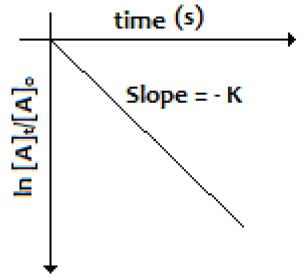
They are reactions with overall order = 1 , for example : **A → P** ----- Rate = $K[A]^1$
The equation which find the concentration of A at any time is :

$$\boxed{\ln [A]_t/[A]_o = -Kt}$$

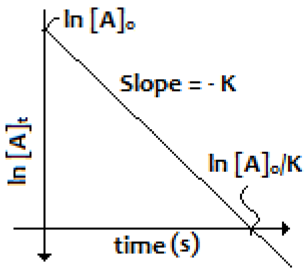
$$\boxed{\ln [A]_t = \ln [A]_o - Kt}$$

ln : logarithm natural اللوغاريتم الطبيعي   t : the time .

As u can see , the first equation is a straight line equation (Y = - aX) :
Y axis → $\ln [A]_t/[A]_o$ while **X axis → t**
the **slope = - K**
X & Y Intercepts = 0 , as shown →→→→→→→→



The second equation is also a straight line equation
(Y = b – aX) :
Y axis → $\ln [A]_t$ while **X axis → t**
the **slope = - K**
Y Intercept (Y when X=0) = $\ln [A]_o$
X Intercept (X when Y=0) = $\ln [A]_o/K$



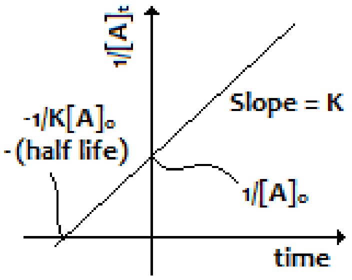
The questions on these diagrams maybe they give u the same diagram with the value of slope & ask for K , or the value of Y intercept & ask for $\ln [A]_o$ & so on .

Second Order Reactions

They are reactions with overall order = 2 , for example : **A → P** ----- Rate = $K[A]^2$

The equation of [A] with time :

$$\boxed{\mathbf{1/[A]_t = 1/[A]_o + Kt}}$$



It's a straight line equation (Y = b + aX) :

$Y = 1/[A]_t$ & **X = t**

the **slope = K** , **Y Intercept = $1/[A]_o$**

the **X intercept = $-1/(K[A]_o)$ = - (half life)** discussed below

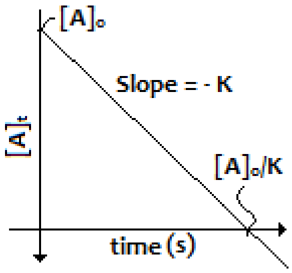
Zero Order reactions

They are reactions with overall order = 0 , for example : A → P

Rate = $K[A]^0$ = K = constant with any A concentration .

The equation of [A] with time :

$$\boxed{\mathbf{[A]_t = [A]_o - Kt}}$$



It's a straight line equation (Y = b – aX) :

$Y = [A]_t$ & **X = t**

the **slope = -K** , **Y intercept = $[A]_o$**

the **X intercept =$[A]_o/K$ =** 2 (half life)

Half Life

- Half life of a reaction (**$t_{1/2}$**) : it's the time required for reactant to become half of its initial concentration .

→ [A] at $t_{1/2}$ = $1/2\ [A]_o$

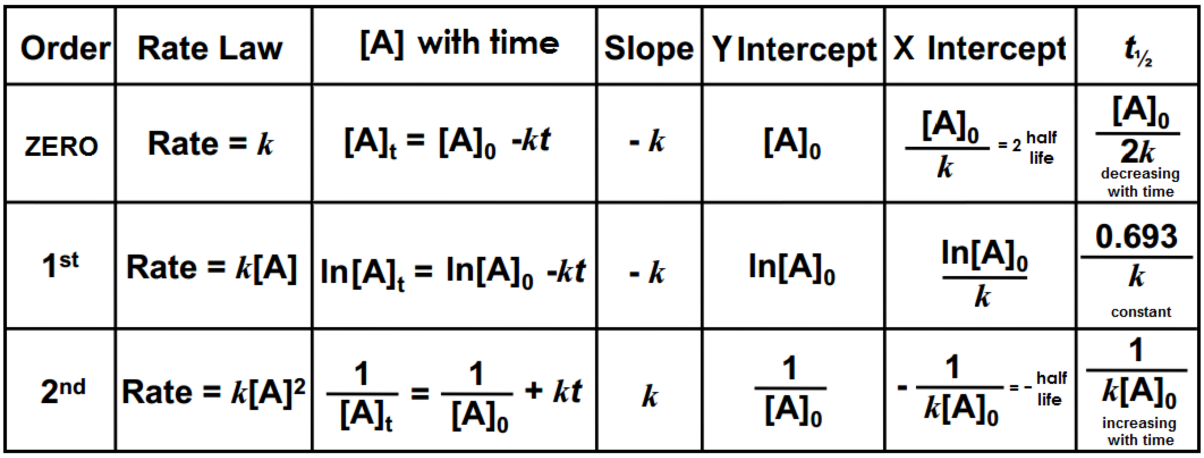
- First Order Reaction Half Life :
  $t_{1/2}$ = 0.693/K constant for each reaction
  (example : if $t_{1/2}$ =50s & $[A]_o$= 100, then :
  (100 M **–50s–>** 50 M **–50s–>** 25 M **–50s→** 12.5 M **–50s→** 6.25 M)

- Second Order Reaction Half Life :
  $t_{1/2}$ = $1/(K[A]_o)$ it increases as the reaction proceeds ($[A]_o$ is decreasing)
  (100 M **–50s–>** 50 M **–100s–>** 25 M **–200s–>** 12.5 M **–400s–>** 6.25 M)

- Zero Order reaction Half Life :

  $t_{1/2} = [A]_o/2K$ it decreases as the reaction proceeds ($[A]_o$ is decreasing)

  (100 M **–400s–>** 50 M **–200s–>** 25 M **–100s–>** 12.5 M **–50s–>** 6.25 M)



Order	Rate Law	[A] with time	Slope	Y Intercept	X Intercept	$t_{½}$
ZERO	Rate = k	$[A]_t = [A]_0 - kt$	$- k$	$[A]_0$	$\frac{[A]_0}{k}$ = 2 half life	$\frac{[A]_0}{2k}$ decreasing with time
1st	Rate = $k[A]$	$\ln[A]_t = \ln[A]_0 - kt$	$- k$	$\ln[A]_0$	$\frac{\ln[A]_0}{k}$	$\frac{0.693}{k}$ constant
2nd	Rate = $k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	k	$\frac{1}{[A]_0}$	$- \frac{1}{k[A]_0}$ = - half life	$\frac{1}{k[A]_0}$ increasing with time

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Examples

- The rate constant for this reaction : **($2A \rightarrow P$)** is $2.667 * 10^{-3}\ s^{-1}$ at 25 °C

  If $[A]_o$ = 2.4 M , **calculate [A] after 5 minutes** .

  Answer : the reaction is 1st order (<u>because of the unit of K</u>) , so :

  $\ln [A]_t = \ln [A]_o – Kt$ → $\ln [A]_t = \ln 2.4 – (2.667 * 10^{-3}$ **$* (5*60)$**)

  → $\ln [A]_t = 0.075$, use the calculator (shift+lin then #) → $[A]_t = 1.08$ M

- Calculate the half life for the previous Qs .

  Answer : $t_{1/2} = 0.693/K$ → $t_{1/2} = 260$ s

- In the previous question , How long will it takes for the concentration of A to decrease from 2.4 to 0.6 M ?

  Answer : 2.4 –260s–> 1.2 –260s–> 0.6 → the time = 260 + 260 = 520s

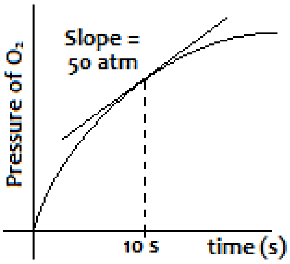
  Or using the equation **:** $\ln 0.6/2.4 = - 2.667*10^{-3} * t$ → t = 520 s

- In the previous question , How long will it takes for the conversion of 87.5% of the starting concentration of A ?

  Answer : $\ln (12.5\% / 100\%) = - 2.667*10^{-3} * t$ → **t = 780 s**

- The rate constant for this reaction : **($2\ NO_2 \rightarrow 2\ NO + O_2$)** is 0.63 $s^{-1}M^{-1}$ at 100 °C . How long will It takes for the concentration of NO_2 to drop from 0.1 M to 0.025 M ?
  Answer : the reaction is 2nd order (because of the unit of K) , so :
  $1/[NO_2]_t = 1/[NO_2]_o + Kt \rightarrow\rightarrow\rightarrow\rightarrow$ t = 47.6 s = **0.79 min**
  (we divide by 60 to convert seconds into minutes)

- In the previous question , Calculate the half life .
  Answer : $t_{1/2} = 1/(K[A]_o) \rightarrow\rightarrow\rightarrow t_{1/2} = 15.9$ s



- u should know that in the exam they may connect the laws of gas pressures (Ideal gas law) with this Chapter laws in three main ways :

  1- Finding the rate of a reaction after being given the changing of pressure per time for a gas in that reaction .
  Example : ($2\ H_2O_2(aq) \rightarrow 2\ H_2O(L) + O_2(g)$**)**
  according to the figure , calculate the rate of the reaction at t = 10 s , if u know that T = 25 °C .
  Answer :
  P = MRT (Ideal Gas Law) → take Δ → $\boxed{\Delta[\ \ ] = \Delta P/RT}$ (because $\Delta M = \Delta[\ \ ]$)
  the slope = $\Delta P/\Delta t$ = 50 atm → **$\Delta P = 50*\Delta t$**
  the Rate = $\Delta[O_2]/\Delta t$ = $(\Delta P/RT)/\Delta t$ = $(50\Delta t/0.0821*298)/\Delta t$ **= 2.04 M/s**

  2- Finding the pressure for a gas in 1st order reactions after a time .
  Example : If u know that the rate constant for this reaction :
  ($SO_2Cl_2 \rightarrow SO_2(g) + Cl_2(g)$ **)** is $4.5 * 10^{-2}\ s^{-1}$ at 660 K .
  What is the pressure of SO_2Cl_2 after 65 s giving that the initial pressure is 375 torr ?
  Answer :
  here u can use this equation : $\boxed{\ln P_t = \ln P_o - Kt}$
  $\rightarrow \ln P_t = \ln(375/760) - 4.5 * 10^{-2} * 65$
  $\ln P_t = -3.63 \rightarrow P_t = 0.0265$ atm = 20.1 torr

3- Finding the pressure for a gas in 2nd order reactions after a time .

here u can use this equation : $\boxed{1/P_t = 1/P_o + Kt}$.

(14.5) Temperature & Rate

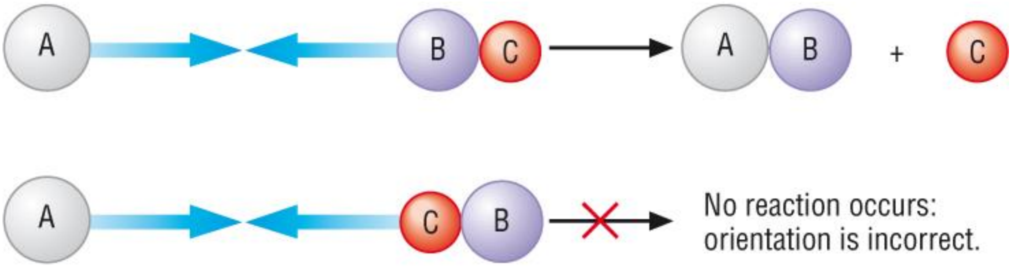
- As we said in the beginning of this chapter , the more temperature , the higher rate , why ?

The Higher Temperature → Higher kinetic energy in the molecules → <u>more collisions</u> → more change of reactants into products → higher rate .

- As a result, with the increase of temperature, the rate constant (K) increases (because it describes the collision rate in that rxn), & vise versa .

- The Collision of molecules which end with products is called an Effective collision . For a collision to be Effective , the Collisional molecules must have two things together :

  1- **True Orientation** (the orientation factor/steric effect) .



  2- Higher kinetic energy than the activation energy .

  Activation Energy (Ea) : minimum amount of energy required to break the existing bonds in the reactants → initiate the reaction .

  * Ea is temperature independent = isn't affected by temperature .

  *** the lower Ea reaction is the faster , & vise versa .**

  (this is the opposite to K , which is T dependant & the higher →faster)

  The activate Complex (transition state) : it is the compound with the highest potential energy among the reactants & products , it has broken bonds of reactants & new formed bonds of products . (transition between reactants & products)

Arrhenius Equation

- It's an equation which connects the activation energy with K of rxn :

$$\boxed{K = A\,e^{-Ea/RT}}$$

$$\boxed{\ln K = \ln A - Ea/RT}$$

$$\boxed{Ea = \ln(A/K) * RT}$$

These are the three forms of Arrhenius equation . K : rate constant .

A : <u>frequency factor</u>/Arrhenius constant (temperature independent)

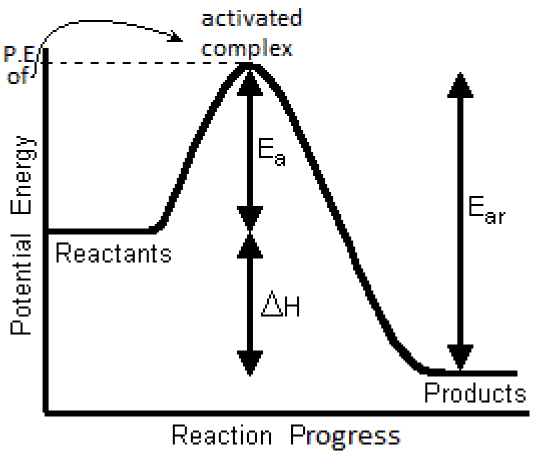
(it refers to frequency of oriented collisions) high A → high K → faster reaction

Ea : activation energy(J/mol) **<u>R : gas constant (8.314 J/mol-K)</u>**

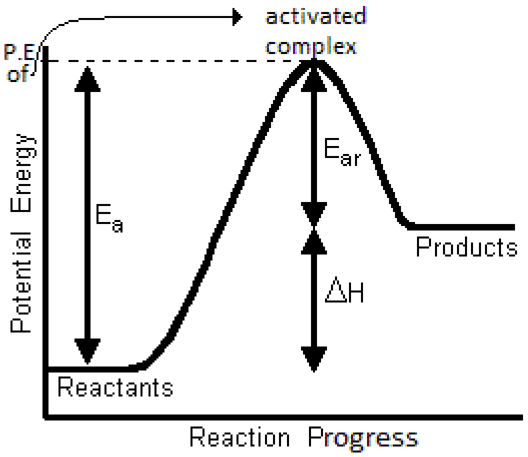
T : in Kelvin

As u know , there are two kinds of reactions , exothermic (gives energy) & endothermic (needs energy) . When we draw the relationship between the potential energy of reactants & products as reaction proceeds , we find :

The Exothermic



The endothermic



Look closer at the figure & notice that :

P.E : potential energy (the energy stored in the bonds of a molecule) .

Ea : the activation energy for the forward reaction .

Ea_r : the activation energy for the reverse reaction .

ΔH : the change in potential energy = the energy lost or required .

- **$Ea =$ P.E(complex) – P.E(reactants) , $Ea_r =$ P.E(complex) – P.E(products)**
- **$\Delta H =$ P.E(products) – P.E(reactants) = $Ea - Ea_r$**
- **$Ea = Ea_r + \Delta H$, $Ea_r = Ea - \Delta H$**

If ΔH for a reaction **is negative → Exothermic ,** if **positive → Endothermic**

- **In Exothermic rxns** : the **forward** rxn is **faster** than the reverse rxn .
- **In Endothermic rxns** : the **forward** rxn is **slower** than the reverse rxn .

- To easily determine whether the figure is for exothermic or endothermic reaction , If the products are less energy than reactants , this indicates that there is a loss in energy → exothermic , & if the energy increased in the products compared to reactants → gain of energy → endothermic .

Example : consider this reaction (A + B → AB) , If P.E for reactants equals 80 J , for products = 20 & for the transition state = 170 J . Find Ea , Ea_r & ΔH , then determine which is faster : the forward reaction or the reverse one .

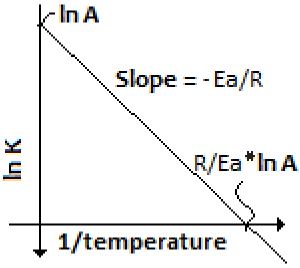
Answer :

Ea = 170 – 80 = 90 J , Ea_r = 170 – 20 = 150 J

ΔH = 20 – 80 = - 60 (→ it's exothermic) , so → the forward is the faster

---

The second form of Arrhenius Equation
(ln K = ln A – Ea/RT) is a linear equation (y = b – aX)
where : y = ln K , X = 1/T
the slope = -Ea/R , y Intercept = ln A →→→→→



- If we have 2 conditions (2 different temperatures so that 2 different rate constants) of a <u>certain reaction (constant A & Ea)</u> then

$$\boxed{\ln (K_1/K_2) = Ea*(T_1 - T_2)/RT_1T_2}$$

K_1 : rate constant at the first temperature (T_1) , K_2 : rate constant at (T_2)

- **Examples :**

- If the rate constant for ($CH_3Cl + H_2O \rightarrow CH_3OH + HCl$) is $3.32 * 10^{-10}$ s^{-1} at 25 °C .
  Calculate the rate constant at 40 °C , If u know that Ea = 116 **<u>Kg</u>**/mol .

  Answer : assume the given K is K_2 & its temperature is (T_2= 298 K) , & the needed K is K_1 & its temperature is (T_1 = 313 K) , then use the law :

$\ln (K_1/K_2) = Ea*(T_1 - T_2)/RT_1T_2$ →
$\ln (K_1/(3.32*10^{-10})) = (\underline{\mathbf{116*1000}})*(15)/(8.314*313*298)$
→ $\ln K_1 - \ln 3.32*10^{-10} = 2.24$ → $\ln K_1 - (-21.825) = 2.24$ → $\ln K_1 = -19.58$
→ shift+ln then put (-19.58) → $K_1 = 3 * 10^{-9}\ s^{-1}$.

- Calculate A at 40 °C for the previous example .
  Answer : K at 40°C = $3*10^{-9}$ → $\ln A = \ln K + Ea/RT$ →
  $\ln A = \ln (3*10^{-9}) + 116000/(8.314*313)$ → $\ln A = 24.95$
  → shift+ln then put (24.95) → $A = 6.86 * 10^{10}$.

- the reaction ($2\ CO + 3\ Cl_2 \rightarrow 2\ COCl_3$) at 250 °C is **$1.5 * 10^3$** times faster than the same reaction at 150°C . Calculate Ea .

  Answer : firstly , suppose that 250 °C = **T_1 = 523 K** , & 150 °C = **T_2 = 423 K**
  Now **Rate1 = $K_1\ [CO]^X\ [Cl_2]^Y$** while **Rate2 = $K_2\ [CO]^X\ [Cl_2]^Y$** , divide them **:**
  rate1/rate2 = $K_1[CO]^X[Cl_2]^Y/K_2[CO]^X[Cl_2]^Y$ →→ rate1/rate2 = **K_1/K_2 = 1500**
  Now use the law **:**
  $\ln (K_1/K_2) = Ea * (T_1 - T_2)/RT_1T_2$ → $\ln 1500 = Ea * (100)/(8.314*523*423)$
  → $7.3 = Ea*5.44*10^{-5}$ →→→ Ea = 134.5 **KJ**/mol .

- given the following reaction : **$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$**
  The rate law for this reaction is first order in each of the two reactants and has a k = 0.0028/M.s at 200°C measured for - d[H2]/dt . Ea for the reaction is 170 kJ/mol. What is the rate of HI formation at 300°C when both H_2 and I_2 are at a concentration of 0.0150 M?
  Answer : the given info :
  first order for H_2 & I_2 → rate = $K\ [H_2]^1[I_2]^1$ → rate = $K\ [H_2][I_2]$
  "measured for - d[H2]/dt " ; means that this K is for the rate of H_2 disappearance , but we know that the rate of H_2 = the rate of reaction because it's 1 mole in the equation (the definition of reaction rate at the beginning of this chapter) → K for disappearance of H_2 = K of the whole reaction , so :
  K at 200 °C = $0.0028\ M^{-1}s^{-1}$
  Ea = 170 kJ/mol , find rate of HI at 300 °C & when $[H_2]=[I_2]= 0.015$ M .

Solving : firstly , rate of HI formation = 2 * rate of reaction (2 moles)

= 2 * K $[H_2][I_2]$

the question wants the rate of HI at 300 ^oC but not at 200 ^oC , so we have 2 conditions : the given condition which is 200^oC → K1 = 0.0028

the needed condition which is 300^oC → K2 = ??

we solve it using the previous equation : **$\ln (K_1/K_2) = Ea*(T_1 – T_2)/RT_1T_2$**

we find K2 from it (it will be 5.29) then we find the rate of HI formation :

rate of HI formation = 2 * K2 $[H_2][I_2]$ = 2 * 5.29 * 0.015 * 0.015 = 0.00238

End Of Chapter 14

Ch.16 **Acid – Base Equilibria**

16.1 **Acids & Bases : A brief Review – Arrhenius definition**

$HCl \rightarrow H^+ + Cl^-$ $NaOH \rightarrow Na^+ + OH^-$

Arrhenius Acids : substances <u>dissolve in water</u> & <u>increase $[H^+]$</u> .

Arrhenius Base : substances <u>dissolve in water</u> & <u>increase $[OH^-]$</u> .

- Arrhenius acids & bases definition is **limited to aqueous solutions** only ,so it isn't good enough .
- In fact , the H^+ ion in water isn't isolated , it reacts completely with water to give Hydronium ion (H_3O^+) so the true form of the first example is :

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

16.2 **Bronsted-Lowry Acids & Bases**

Bronsted acid : substance that donates a proton (H^+ ion) to another one .

Bronsted Base : substance that accepts a proton (H^+ ion) from the acid .

Examples :

$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$

(HCl is the acid because it gives H^+ , H_2O is the Base because it accepts it)

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

(H_2O is the acid because it gives H^+ , NH_3 is the Base because it accepts it)

- Bronsted acids & bases definition includes the Arrhenius definition , but it isn't limited to aqueous solutions , so it's a generalized rule

- If u focus on the previous 2 examples , the water molecule in the first one plays as a base , while in the second ,it plays as an acid , these such substances are called : **Amphiprotic** or **Amphoteric** substance .
  Example for these substances are the **Anions with H^+ able to donate** , like : HCO_3^- , HSO_3^- , OH^-.

Conjugate acid-base pairs

- In all acid-base reactions ,there are acid & base in the reverse reaction in addition to the ones in the forward reaction , & they are called : **conjugate acid** & **conjugate base** .
- The acid & it's conjugate base or the base with its conjugate acid are called: **conjugate acid-base pair .**

Examples :

$HNO_2 + H_2O \leftrightarrows NO_2^- + H_3O^+$

(Acid : HNO_2 , Base : H_2O , Conjugate Acid : H_3O^+ , Conj. Base : NO_2^-)

conjugate acid-base pairs : (HNO_2 - NO_2^-) & (H_2O - H_3O^+) .

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

(Acid : H_2O , Base : NH_3 , Conj. Acid : NH_4^+ , Conj. Base : OH^-)

conjugate acid-base pairs : (NH_3 - NH_4^+) & (H_2O - OH^-) .

- To determine the conjugate acid/base for a molecule/Ion , use this hint :
  1- asking about conj. Acid means that the given molecule is a base , so it accepts H^+ → the conj. Acid is the given molecule with H^+ :
  Example : find the conjugate Acid for : O^{-2} , H_2O , $H_2PO_4^-$, $HCOO^-$
  Answer : the conj. acids : OH^- , H_3O^+ , H_3PO_4 , HCOOH

  2- asking about conj. Base means that the given molecule is an acid , so it donates H^+ → the conj. Base is the given molecule without H^+ :
  Example : find the conjugate Base for : OH^- , HCN , HPO_4^{-2} , HCO^+
  Answer : the conj. base : O^{-2} , CN^- , PO_4^{-3} , CO

- The most successful Definition for Acids & Bases is the **Lewis definition** (it's section 16.11), it states that :
  For a molecule to behave as a base , it must have at least one non-bonding Pair of Electrons ,(like : **NH_3 , H_2O , H_2S , F^- , O^{-2} , H^- ,CH_3^- , N^{-3}**)
  why ? → to donate this pair & make a bond with H^+ (<u>or any molecule has an empty orbital in its outer most shell</u>, like B compounds–example BF_3-)
  The benefit of this definition is that we can determine if this compound is an acid or base without knowing its reaction , by knowing its structure only . while other definitions require the reaction of the compounds .
  so as a result , the Lewis definition is summarized as :
  1- **Lewis Base** : electrons pair ($2e^-$) donor , which makes a bond with empty orbital molecule . (any molecule have $2e^-$, **most anions**)
  2- **Lewis Acid** : electron pair ($2e^-$) acceptor , which have an empty orbital to accept the $2e^-$ (the bond) . (H^+ , **most cations** , & Be,B,Al compounds)

16.3 **The Auto-Ionization Of Water**

- The Auto-Ionization Of Water **means** : donating a proton from one water molecule to another :

$H_2O \leftrightarrows H^+ + OH^-$, but All H^+ with water makes H_3O^+ ($H^+ + H_2O \rightarrow H_3O^+$)
so in overall : **$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$**
this Ionization is very little , (there are only 2 ionized molecules out of billion water molecules at 25 °C)

- (H_3O^+) is (H^+) in water , so if u were asked for $[H^+]$, it's equal to $[H_3O^+]$.

$$\boxed{K_W = [H_3O^+][OH^-]}$$

K_W : the equilibrium constant / Ion product constant for water , it is **temperature dependant** (has different values at different temperatures) .
At 25 °C → $K_W = 1 * 10^{-14}$ = $[H_3O^+][OH^-]$

- The previous Equation is also applicable to aqueous solutions (in addition to pure water) , so next sections (Acids & Bases solutions) we can use this equation to calculate $[H_3O^+]$ from $[OH^-]$ & vise versa , of acid or base solution . **at 25 °C → $K_W = 10^{-14}$** = $[H_3O^+][OH^-]$, so :

$\boxed{[H_3O^+] = 10^{-14}/[OH^-]}$ **&** $\boxed{[OH^-] = 10^{-14}/[H_3O^+]}$

- **IF $[H_3O^+] = [OH^-]$** = 10^{-7} M → pure water or neutral solution
  IF $[H_3O^+] > [OH^-]$, Or $[H_3O^+] > 10^{-7}$ M , Or $[OH^-] < 10^{-7}$ M → acidic soln
  IF $[OH^-] > [H_3O^+]$, Or $[OH^-] > 10^{-7}$ M , Or $[H_3O^+] < 10^{-7}$ M → Basic soln

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16.4 **The pH Scale**

- The "p" in "pH" means (–log) , while the "H" refers to H^+ concentration (which equals $[H_3O^+]$) so :

$$\mathbf{pH = -\log [H_3O^+]} \quad \leftrightarrow \quad [H_3O^+] = 10^{-pH}$$

the pH is a measure of the Acidity of a solution . **The less pH → the more acidic** ($[H_3O^+] > [OH^-]$) , while the more pH →the more basic ($[OH^-] > [H_3O^+]$) .

At 25 ºC , the neutral aqueous solution has a **pH = 7** , the acidic has a **pH < 7** , the basic has a **pH > 7** .

Question : Calculate $[H^+]$ for apple juice which has a pH of 3.76 .
Answer : $[H_3O^+] = 10^{-pH}$, $[H_3O^+] = 10^{-3.76} = 1.7 * 10^{-4}$ M

Question : Calculate pH for a solution has $[H_3O^+] = 4.2 * 10^{-4}$ M .
Answer : **$pH = -\log [H_3O^+]$** , $pH = -\log (4.2 * 10^{-4}) = 3.38$.

Question : Calculate pH for a solution has $[OH^-] = 1.9 * 10^{-6}$ M at 25 ºC .
Answer : $[H_3O^+] = 10^{-14}/[OH^-]$ →→ $[H_3O^+] = 5.3 * 10^{-9}$ M → **$pH = -\log [H_3O^+]$**
→→→ pH = 8.28

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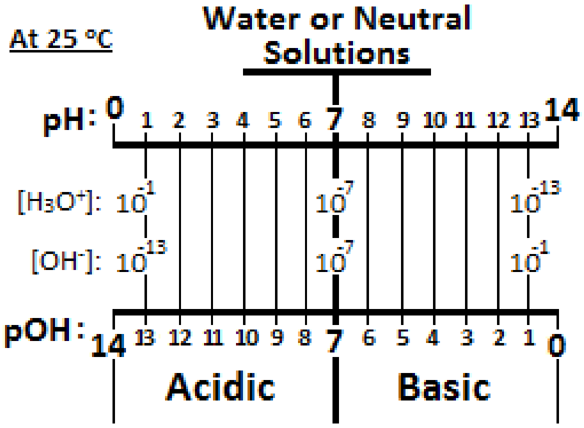
pOH & other p scales

- As we said , the "p" means –log , so to measure the Basicity of a solution , we use pOH :

$$\mathbf{pOH = -\log [OH]} \quad \leftrightarrow \quad [OH^-] = 10^{-pOH}$$

The less pOH the more basicity , the more pOH the more acidity .

At 25 ºC , the neutral solution has a **pOH = 7** , the Basic has a **pOH < 7** , the Acidic has a **pOH > 7** .



- As u see from the figure, **pH + pOH = 14** always (at 25 °C) , 14 is the **pK_W .**
  pK_W = –log K_W (at 25 °C → pK_W = -log 10^{-14} = **14**) so :

$\boxed{pH + pOH = pK_W}$ & at 25 °C : $\boxed{pH = 14 - pOH}$ & $\boxed{pOH = 14 - pH}$

Question : If the pOH for a solution is 3 , find : pH , $[OH^-]$ & $[H_3O^+]$.
& determine whether the solution is acidic or basic . **its basic**

Answer : pH = 14 - pOH =14 - 3= 11 ,**$[OH^-] = 10^{-pOH}$**$= 10^{-3}$,**$[H_3O^+] = 10^{-pH}$**$= 10^{-11}$

Question : Rank the following solutions according to their acidity .

1) solution of 3.7 pH 2) solution of $5*10^{-4}$ $[H_3O^+]$
3) solution of 8 pOH 4) solution of $8.5*10^{-13}$ $[OH^-]$.

Answer : to compare them , we must convert them to one variable (pH , pOH ,$[OH^-]$ or $[H_3O^+]$) , I will convert them to $[H_3O^+]$:

1) $[H_3O^+]= 10^{-3.7}= 2*10^{-4}$ M 2) $[H_3O^+] = 5*10^{-4}$ M
3) $[OH^-]=10^{-8}$ → $[H_3O^+] = K_W/[OH^-] = 10^{-14}/10^{-8} = 10^{-6}$ M
4) $[H_3O^+] = 10^{-14}/(8.5*10^{-13}) = 1.2 * 10^{-2}$ M

so : higher $[H_3O^+]$ more acidic →→ **4 > 2 > 1 > 3**

Acid-Base Strength

- **Acidity :** the ability to donate a proton (H^+) .
  the higher this ability → the higher acidity (stronger acid) .
- **Basicity :** the ability to accept a proton (H^+) .
  the higher this ability → the higher basicity (stronger base) .

  - the stronger the acid , the weaker the conjugate base .
  - the stronger the base , the weaker the conjugate acid .

16.5 **Strong Acids & Bases**

Strong Acids/Bases has a **100% dissociation** , means that they are completely Ionized in aqueous solutions . they have a **<u>very weak</u> conjugate bases/acids** .

Strong Acids

1- Monoprotic acids : have 1 protons able to donate . they are 6 : (HCl, HBr, HI, HNO_3, $HClO_4$, $HClO_3$) .

2- Diprotic acid : have 2 protons able to donate , it's the (H_2SO_4) only . Only the first proton dissociates completely while we deal with the second proton as if (HSO_4^-) is a weak acid (next section) & in the solution when we want to calculate $[H_3O^+]$ or pH , we treat it as if it was Monoprotic (we don't say that the result is 2 protons but 1 proton) , & we use the following laws , because the second proton dissociates very little & we neglect it .

Because the dissociation is 100% → **$[H_3O^+]$ = [conj. Base] = $[Acid]_o$**
($[Acid]_o$: Initial concentration) so :

$$\boxed{pH = -\log [Acid]_o} \quad \leftrightarrow \quad \boxed{[Acid]_o = 10^{-pH}}$$

Examples on the strong acids :
Question : Calculate the pH for $1*10^{-4}$ HCl aqueous solution .
Answer : pH = -log[HCl] = -log ($1*10^{-4}$) = 4

Question : Calculate pOH for $3.64 * 10^{-2}$ $HClO_3$ aqueous solution .
Answer : pOH = 14 – pH = 14 + log [$HClO_3$] = 14 + log ($3.64 * 10^{-2}$) = 14 - 1.44
= 12.56

Question : What is the initial concentration of HNO_3 acid , if the pH of its solution equals 2.34 .
Answer : $[HNO_3]_o = 10^{-pH} = 10^{\mathbf{-2.34}} = 4.6 * 10^{-3}$ M

Question : What is the concentration of ClO_3^- in 3 M $HClO_3$ solution? → 3 M

Question : What is $[ClO_3^-]$ in $HClO_3$ solution which has pH = 4 ?
Answer : $[ClO_3^-] = [Acid] = 10^{-pH} = 10^{-4}$.

Question : Calculate pH for solution made by mixing 100 mL of 0.1 M HBr & 50 mL of 0.5 M HNO_3 .

Answer : if u remember from the first exam summary :

M(H^+) after mixing strong acids = $\frac{(MV)1+(MV)2}{V1+V2}$, which means :

$\boxed{[H_3O^+] = \frac{(MV)1+(MV)2}{V1+V2}}$ = (0.1*0.1 + 0.5*0.05)/(0.1+0.05) = 0.23 M

→ pH = - log $[H_3O^+]$ = - log 0.23 = 0.64

Strong Bases

- They are **Hydroxides** (OH^-) , **Hydrides** (H^-) , **Oxides** (O^{-2}) & **Nitrides** (N^{-3}) bonded to the elements of **1A & 2A Groups** (except Be, Mg ,Fe) .

  meaning that the $Be(OH)_2$ isn't strong base , the same as $Mg(OH_2)$, $Fe(OH)_2$,,, & the 3A elements don't make strong bases , example : $Al(OH)_3$ which is weak base (next sections)

- The most <u>soluble</u> Strong Bases are the hydroxides with 1A :

  LiOH , NaOH , KOH , RbOH
- The strength of hydrides (H^-) > Oxides (O^{-2}) > hydroxides (OH^-) .
- The Hydroxides directly give OH^- ions , while others don't :

  1- Hydrides : $NaH + H_2O \rightarrow Na^+ + H_2 + OH^-$, How ??

  firstly, NaH dissociates: $NaH \rightarrow Na^+ + \mathbf{H^-}$, then H^- reacts with water : $H^- + H_2O \rightarrow H_2 + OH^-$. so in overall we get the previous equation .

  2- Oxides : $BaO + H_2O \rightarrow Ba^{+2} + 2\,OH^-$

  $BaO + H_2O \rightarrow Ba^{+2} + O^{-2}$,,,, then : $O^{-2} + H_2O \rightarrow 2\,OH^-$.

  3- Nitrides : $N^{-3} + 3\,H_2O \rightarrow NH_3 + 3\,OH^-$

- To solve the Questions on the strong bases ,we must consider the # of resulted (OH^-) from the base dissociation , I will call this # : (i) , Then :

$$\boxed{pOH = -\log i*[Base]_o} \quad \leftrightarrow \quad \boxed{[Base]_o = 10^{-pOH}/ i}$$

- **Without writing the equation of the reaction** :

  i = the # of **(OH) or (H)** in hydroxides & hydrides **= 2***# of **(O)** in oxides = 3*# of (**N**) in nitrides .

for example: $Ca(OH)_2$ → i = 2 , $Ba(H)_2$ → i = 2 , K_2O →(# of O =1)→ i = 2

Li_3N → i = 3

Examples on the strong Bases :

Question : Calculate pH for 0.028 M solution of NaOH .

Answer : pOH = -log i*[NaOH] = -log 1*(0.028) = 1.55 then :

pH = 14 – pOH = 12.45

Question : Calculate pH for 0.0011 M solution of $Ca(OH)_2$.

Answer : in the same way **but i = 2** not 1→→→ pH = 11.34

Question : What is the Concentration of $Ca(OH)_2$ sample , if its solution has a pH of 11.68 .

Answer : find pOH → pOH = 14 – pH = 2.32 , then :

$[Ca(OH)_2] = 10^{\mathbf{-pOH}}/ i = 10^{\mathbf{-2.32}}/2 = 0.0024$ M

Question : what is the pH of 0.01 M Na_2O solution ?

Answer : i = 2 (because O = 1 & we multiply with 2 as I mentioned above)

Now : pOH = -log i*[Na_2O] →→→ then use : pH = 14 – pOH

→→→→ result : pH = 12.3

Very important Note : For Strong Acids & bases , actually when we add them to water → $[H_3O^+]$ soln = $[H_3O^+]$ water + $[H_3O^+]$ from the acid/base

but because $[H_3O^+]$ from water is 10^{-7} (at 25 °C) which is very small comparing to $[H_3O^+]$ from the acid/base , we neglect it & only consider that of the strong acid or base .

BUT if $[H_3O^+]$ from the acid/base is < 10^{-7} → the $[H_3O^+]$ from water becomes higher than that from acid/base , so we consider the $[H_3O^+]$ from water & neglect that of the strong acid/base , so pH = -log 10^{-7} = **7** , which means the soln is neutral (the very tiny amount of acid/base is negligible) .

Example : the pH of $1*10^{-10}$ M HCl solution at 25 °C is :

a) 10 b) 4 c) 7 D) 5

Answer : $[H_3O^+]$ from HCl = [HCl] = 10^{-10} which is < 10^{-7} so we take the $[H_3O^+]$ coming from auto-ionization of water = 10^{-7} →→→ pH = 7 **(c)**

Weak Acids & Weak Bases

- They partially react with water & reach equilibrium , so they have less than 100 % dissociation . they have **weak conjugate Bases/Acids** .

16.6 **Weak Acids**

- They are any compound has a proton (H^+) able to loss , & not a strong acid
- **Examples : HF** , **CH_3COOH** , HClO , $HClO_2$, **HCN** , **HNO_2** , H_2S
  NH_4^+ , $CH_3NH_3^+$
  HSO_4^- which is come from H_2SO_4

- Weak acids have < 100% dissociation , means that they are partially ionized in aqueous solutions → have an **equilibrium equation**

- We deal with the weak acids like our dealing with water auto-ionization , the weak acid equilibrium gives very little protons to the water molecules forming H_3O^+ , as the following :
  $HA \leftrightharpoons \mathbf{H^+} + A^-$, then $\mathbf{H^+} + H_2O \rightarrow H_3O^+$, in overall : $\boxed{\mathbf{HA + H_2O \leftrightharpoons H_3O^+ + A^-}}$

(HA is the weak acid , A^- is the conjugate base of the weak acid)

- The equilibrium constant for the previous equation is called K_a :

$$\boxed{K_a = \frac{[H3O+][A-]}{[HA]eq}}$$

(**K_a : acid-dissociation constant / equilibrium constant for an acid**)

- K_a indicates the tendency of the acid to ionize in water (the acidity) , so :
  the more K_a for weak acid → the stronger the acid , meaning that :
  (higher the acidity & lower the basicity) And
  (higher $[H_3O^+]$, lower $[OH^-]$ & lower pH for the acids of equal conc.)

(**$[HA]_{eq}$: the concentration of HA at equilibrium , not the initial one**)

What do we mean by "the concentration of HA at equilibrium" ??
→ As we said , weak acids dissociate partially , so [HA] at equilibrium decreases slightly from the initial concentration , on the other hand $[H_3O^+]$ & $[A^-]$ both increase by the same decrease of [HA] , as the following :

$HA + H_2O \leftrightarrows H_3O^+ + A^-$

Concentrations at the beginning : $[HA]_o$ 0 0

Concentrations at equilibrium : $([HA]_o - X) \leftrightarrows X$ X

- so $\boxed{[H_3O^+] = [A^-] = X}$ & all are **< $[HA]_o$** , $\boxed{[HA]_{eq} = ([HA]_o - X)}$

Now we have 2 Cases :

1- assuming that $[HA]_{eq} = [HA]_o$,only when X is negligible comparing to $[HA]_o$

then use these laws : $\boxed{K_a = \frac{[H3O+][A-]}{[HA]o}}$ → $\boxed{[H_3O^+] = \sqrt{Ka * [HA]o}}$

2- solving in quadratic equation , when X can't be neglected (large) .

we start by trying to solve one of these equations :

$$\boxed{K_a = X^2/([HA]_o - X)} \leftrightarrow \boxed{[HA]_o = (X^2/K_a) + X}$$

We determine whether the value of X is negligible or not , according to something called : the $\boxed{\textbf{percent Ionization} = [H_3O^+]/[HA]_o * 100\%}$

If % Ionization < 5% → neglect X → $[HA]_{eq} = [HA]_o$

but If it was > 5 % → don't neglect X → $[HA]_{eq} = [HA]_o - X$

If u focus on this law , u will conclude that we can't find % ionization unless we know the $[H_3O^+]$, so we can't know whether to neglect X or not in the beginning of the question , which means that this law is useless from this aspect .

- I know ur feelings now because of this hell :P ,,, for this reason , I myself made a Law to clear everything & to direct calculations for all what is required from weak acids & bases without using the quadratic equation which is time-consuming & somehow hard for many students , this Law is my best useful derived Law I have ever derived .
  I hope no one steal it :'(.

  firstly , to determine whether we neglect X or not from the beginning of any question (% of ionization is unknown & can't be measured) :
  calculate $[HA]_o/K_a$, then

- If it was **> 380 → neglect X** → use $\boxed{[H_3O^+] = \sqrt{Ka * [HA]o}}$, $\boxed{K_a = X^2/[HA]_o}$
- If it was **< 380 → don't neglect X** → Use this Law :

calculate F → $\boxed{F = \sqrt{0.25 + [HA]o/Ka} - 0.5}$, then :

$[H_3O^+] = FK_a$, pH = – log (FK_a) , % Ionization = ($FK_a/[HA]_o$)*100%

- As a summary for all laws of weak acids :

  1- If the % ionization < 5% Or the $[HA]_o/K_a > 380$) → we neglect X :
  we use these laws :

  $\boxed{K_a = X^2/[HA]_o}$, $\boxed{[HA]_o = (X^2/K_a) = [HA]_{eq}}$, $\boxed{[H_3O^+] = \sqrt{Ka * [HA]o}}$

  $\boxed{\% \text{ ionization} = \frac{[H3O+]}{[HA]o} *100\% = \sqrt{\frac{Ka}{[HA]o}} *100\%}$, pH = - log $[H_3O^+]$

  2- If the % ionization > 5% Or the $[HA]_o/K_a < 380$) → we don't neglect X :
  we use these laws :

  $\boxed{K_a = X^2/([HA]_o - X)}$, $\boxed{[HA]_o = (X^2/K_a) + X = [HA]_{eq} + X}$, $\boxed{[H_3O^+] = FK_a}$

  $\boxed{\% \text{ ionization} = \frac{[H3O+]}{[HA]o} *100\% = \frac{FKa}{[HA]o} *100\%}$, $\boxed{pH = -\log (FK_a)}$

- **Note** (just to know) : when $[HA]_o/K_a = 380$, the % ionization is exactly 5%
  when it's >380 the % ionization is < 5% , when < 380 the % ionization is >5%
  I found this during the derivation :D .

Examples on the weak acids

Question : If we have a 0.10 M solution of HCOOH with pH of 2.38 . Calculate K_a of HCOOH .

Answer : $[H_3O^+] = 10^{-pH} = 10^{-2.38} = 0.00417 = X$ then :

$$K_a = X^2/([HA]_o - X) = 1.8 * 10^{-4}$$

(If the Question mentions one of ($[HA]_o$, K_a) & asks for the another , then use : **$K_a = X^2/([HA]_o - X)$** , which means don't neglect X value)

Question : A solution of HNO_2 in H_2O has a pH of 10.5 , what is the initial concentration of HNO_2 ??? ($K_a = 4.5 * 10^{-4}$)

Answer : here gives K_a & asks for $[HA]_o$, so don't neglect X .

$[H_3O^+] = 10^{-pH} = 10^{-10.5} = 3.16 * 10^{-11} = X$

use $[HA]_o = (X^2/K_a) + X = 3.16 * 10^{-11}$ M

Question : A 0.1 M solution of (HF) , contains 4.2 * 10^{-3} **H^+**(*aq*) .
Calculate the % Ionization .

Answer : % Ionization = $[H_3O^+]/[HF]_o$ * 100% = 4.2*10^{-3}/0.1 *100% = 4.2%

Question : Calculate the pH of a 0.2 M solution of HCN (K_a = 4.9 * 10^{-10})

Answer : to find pH , we need $[H_3O^+]$. now to determine whether to neglect X or not → use my note previously :

$[HCN]_o/K_a$ = 0.2/(4.9*10^{-10}) which is > 380 → neglect X

so $[H_3O^+]$ = $\sqrt{Ka * [HA]o}$ →→→ $[H_3O^+]$ = 9.9 * 10^{-6} M →→ pH = 5

Question : Calculate the percentage of HF molecules ionized in :

a) 0.1 M HF solution . b) a 0.010 HF solution . (K_a of HF = 6.8*10^{-4})

Answer :

a) $[HF]_o/K_a$ = 0.1/(6.8*10^{-4}) = 147.06 which is < 380 → don't neglect X :

F = $\sqrt{(\mathbf{0.25} + [\mathbf{HF}]./\mathbf{Ka})}$ **- 0.5** = $\sqrt{0.25 + 147.06} - 0.5 = \mathbf{11.64}$

% Ionization = $FK_a/[HF]_o$ * 100% = (11.64*6.8*10^{-4}/0.1) *100% = 7.9 %

b) $[HF]_o/K_a$ = 0.01/(6.8*10^{-4}) = 14.706 → < 380 → don't neglect X :

F = $\sqrt{(\mathbf{0.25} + [\mathbf{HF}]./\mathbf{Ka})}$ **- 0.5** = $\sqrt{0.25 + 14.706} - 0.5 =$ **3.367**

% Ionization = 100* $FK_a/[HF]_o$ % = 100*3.367*6.8*10^{-4}/0.01 % = 22.9 %

**** **the % Ionization decrease with the increase of $[HA]_o$ & vise versa .**

Question : Rank the following according to their % Ionization :

1- 0.001 M of HCl 2- 0.12 M of HF 3- 0.5 M of HF 4- 1 M of HF

Answer : HCl is a strong acid → 100% ionization
HF is a weak acid , so less [HF] → higher % ionization .
so the ranking is : 1 > 2 > 3 > 4

Polyprotic Weak Acids

- The previously mentioned weak acids were Monoprotic weak acids .
- Now we will talk about the **Polyprotic weak acids** (have more than 1 proton able to loss) **, & they are :**

1- $\boxed{\mathbf{H_2SO_3}\text{ , }\mathbf{H_2CO_3}\text{ \& }\mathbf{H_3PO_4}}$ 2- $H_2C_2O_4$, $H_2C_4H_4O_6$, $H_2C_6H_6O_6$ & $H_3C_6H_5O_7$

- For these weak acids , there are more than one K_a ,,, according to the # of protons the weak acid have , the # of K_a be .
  for example , **H_2SO_3 , H_2CO_3** , $H_2C_2O_4$, $H_2C_4H_4O_6$, $H_2C_6H_6O_6$,,, all of them have 2 protons , so each one of them have 2 K_a (K_{a1} & K_{a2}) , while **H_3PO_4** & $H_3C_6H_5O_7$ have 3 protons , so they have 3 K_a (K_{a1} , K_{a2} & K_{a3})

- What do we mean by K_{a1} , K_{a2} & K_{a3} ??
  K_{a1} is the acid-dissociation constant for the first proton
  K_{a2} is the acid-dissociation constant for the second proton
  K_{a3} is the acid-dissociation constant for the 3rd proton

- Let's have H_2SO_3 as an example for better understanding :
  in the aqueous solution of this acid , we have the following 2 reactions :
  $H_2SO_3 + H_2O \leftrightarrows HSO_3^- + H_3O^+$ ------------------- 1st proton dissociation (K_{a1})
  then the HSO_3^- ,which is also weak acid, will react with water :
  $HSO_3^- + H_2O \leftrightarrows SO_3^{-2} + H_3O^+$ -------------------- 2nd proton dissociation (K_{a2})

  now H_2SO_3 is partially ionized to give HSO_3^- (so that the # of HSO_3^- is small) & then HSO_3^- also is partially ionized , as a result , the H_3O^+ which comes from HSO_3^- is very small & negligible in most cases .
  also u should know that the neutral acids easily donate their protons while the anion acids are harder to donate their protons (because they have a basic character –they are **amphiprotic**- which makes them relatively bad acids)

  As a result , K_{a2} is much less than K_{a1} ,,, & K_{a3} is surely the least .

- **Rule** : for polyprotic weak acids (H_2A) , **If $K_{a1}/K_{a2} > 1000$** , then :
  1- the **total $[H_3O^+]$** in the solution of Polyprotic acids is the $[H_3O^+]$ which comes from the first proton dissociation only (the other dissociation is neglected) . so $\boxed{[H_3O^+]_{total} = [H_3O^+]_1}$
  2- $\boxed{[A^{-2}] = K_{a2}}$

- For (H_3A) polyprotic weak acids :
  If $\mathbf{K_{a1}/K_{a2} > 1000}$, then $\mathbf{[H_3O^+]_{total} = [H_3O^+]_1}$ & $\mathbf{[HA^{-2}] = K_{a2}}$
  If $\mathbf{K_{a2}/K_{a3} > 1000}$, then $\mathbf{[A^{-3}] = K_{a3}}$

- To calculate $[H_3O^+]_1$, we solve as we solved in the Monoprotic weak acids (the section before this) :
  if $[acid]_o/K_{a1} > 380$ → $\mathbf{[H_3O^+] = \sqrt{Ka * [HA]o}}$
  if $[acid]_o/K_{a1} < 380$ → $\mathbf{[H_3O^+] = FK_{a1}}$ $(F = \sqrt{0.25 + [HA]o/Ka} - 0.5)$
  → $\mathbf{pH = pK_{a1} - \log F = -\log (FK_{a1})}$

Examples :

- Calculate the pH of a 10 M H_2SO_3 solution .
  (given that $K_{a1} = 1.7*10^{-2}$, $K_{a2} = 6.4 * 10^{-8}$)
  Answer : $K_{a1}/K_{a2} >> 1000$ → $\mathbf{[H_3O^+]_{total} = [H_3O^+]_1}$
  $[H_2SO_3]_o/K_{a1} >> 380$ → $\mathbf{[H_3O^+] = \sqrt{Ka * [HA]o}} = 0.4123$
  $pH = -\log [H_3O^+] = -\log 0.4123 = 0.3845$

- Calculate the pH of the solution of 0.1 M H_3PO_4 , then calculate the concentration of PO_4^{-3} in it .
  (given that $K_{a1} = 7.5 * 10^{-3}$, $K_{a2} = 6.2 * 10^{-8}$, $K_{a3} = 4.2 * 10^{-13}$)
  Answer : $K_{a1}/K_{a2} >> 1000$ → $\mathbf{[H_3O^+]_{total} = [H_3O^+]_1}$
  $[H_3PO_4]_o/K_{a1} = 13.33 < 380$ → $\mathbf{pH = -\log (FK_{a1})}$
  $(F = \sqrt{0.25 + [HA]o/Ka} -0.5 = \sqrt{0.25 + 13.33} -0.5 = 3.19)$
  → $pH = -\log (FK_{a1}) = -\log 0.0239 = 1.62$
  → $K_{a2}/K_{a3} >> 1000$ → $[PO_4^{-3}] = [A^{-3}] = K_{a3} = 4.2 * 10^{-13}$

(16.7) Weak bases

- They are compounds that partially accept a proton from water leading to formation of some OH^- ions in **equilibrium reaction** , they are :
  1- ammonia (NH_3) , amines (CH_3NH_2) & (C_5H_5N) . ***the most common***
  2- the anions of Monoprotic weak acids (F^- , CH_3COO^- , ClO^- , CN^- , HS^-) .
  3- the anions of polyprotic weak acids (SO_3^{-2} ,HSO_3^- , CO_3^{-2},HCO_3^- , PO_4^{-3}) .
  - H_2S is also weak base , it is an amphiprotic molecule .

- All of them have at least 1 lone pair of electrons (non-bonding electrons) needed to form bond with H^+ .

- So in aqueous solutions of weak bases , the equilibrium reaction of any weak base is as the following : $B + H_2O \leftrightarrows BH^+ + OH^-$ (B : weak base)
  - The equilibrium-constant for the reaction of weak bases is the K_b :

$$K_b = \frac{[BH+][OH-]}{[B]eq}$$

(K_b : base-dissociation constant , $[B]_{eq}$: base concentration at equilibrium)

- Let's have a look to what happen during reaction :

	$B + H_2O \leftrightarrows$	BH^+	$+ OH^-$
Concentrations at the beginning :	$[B]_o$	0	0
Concentrations at equilibrium :	$([B]_o - X) \leftrightarrows$	X	X

- $\boxed{[BH^+] = [OH^-] = X}$ **<<< $[B]_o$** , $\boxed{[B]_{eq} = [B]_o - X}$

- As we said in weak acids , we have 2 cases :

  1- If the % ionization < 5% Or the **$[B]_o/K_b > 380$** → we neglect X :
  we use these laws :

  $\boxed{K_b = X^2/[B]_o}$, $\boxed{[B]_o = X^2/K_b} = [B]_{eq}$, $\boxed{[OH^-] = \sqrt{Kb * [B]o}}$

  $\boxed{\% \text{ ionization} = \frac{[OH-]}{[B]o} * 100\% = \sqrt{\frac{Kb}{[B]o}} * 100\%}$, $\boxed{pOH = -\log [OH^-]}$

  2- If the % ionization > 5% Or the **$[B]_o/K_b < 380$** → we consider X :
  we use these laws :

  $\boxed{K_b = X^2/([B]_o - X)}$, $\boxed{[B]_o = (X^2/K_b) + X} = [B]_{eq} + X$, $\boxed{[OH^-] = FK_b}$

  $\boxed{\% \text{ ionization} = \frac{[OH-]}{[B]o} * 100\% = \frac{FKb}{[B]o} * 100\%}$, $\boxed{pOH = -\log (FK_b)}$

($\boxed{F = \sqrt{0.25 + [B]o/Kb} - 0.5}$)

Examples on weak bases :

Question : Calculate the pH & the molar concentration of $C_2H_5NH_2$, $C_2H_5NH_3^+$ & OH^- at equilibrium , for 0.75 M $C_2H_5NH_2$ solution .
(given that $K_b = 6.4 * 10^{-4}$)

Answer : $[B]_o/K_b = 1172 > 380$ → neglect X :

$[OH^-] = [C_2H_5NH_3^+] = \sqrt{Kb * [B]o} = 0.022$ M

pH = 14 – pOH = 14 – (- log 0.022) = 12.34

$[C_2H_5NH_2]_{eq} = [C_2H_5NH_2]_o - X = 0.75 - 0.022 = 0.728$ M

Question : A solution of NH_3 in water has a pH of 10.5 . what is the molarity of this solution ?? (given that $K_b = 1.8 * 10^{-5}$)

Answer : the molarity of the solution means the $[NH_3]_o$ in this solution .

we are dealing with base , so we find pOH firstly :

pOH = 14 – pH = 14 – 10.5 = 3.5

→ $[OH^-] = 10^{-pOH} = 10^{-3.5} = 3.16 * 10^{-4}$

Now we use : $\mathbf{[NH_3]_o = (X^2/K_b) + X} = (3.16 * 10^{-4})^2/(1.8 * 10^{-5}) + 3.16 * 10^{-4}$
$= 5.8635$ M

Question : A solution made by adding NaClO to enough water to make 2L of solution has a pH of 8.5 . How many moles of NaClO were added to the water to make this solution ? (giving that K_b of $ClO^- = 3.3 * 10^{-7}$)

Answer : NaClO is a salt , so it dissociates 100% in water giving ClO^- with the same concentration ($NaClO \rightarrow Na^+ + ClO^-$) , which will react partially with water as a weak base : $ClO^- + H_2O \leftrightarrows HClO + OH^-$.
we need the moles of NaClO , so we firstly should find its concentration :
$[NaClO] = [ClO^-]_o = (X^2/K_b) + X$,,,,,, but $X = [OH^-] = 10^{-pOH} = 10^{-(14-pH)} = 10^{-5.5}$
$= 3.16 * 10^{-6}$ M
→$[NaClO] = [ClO^-]_o = (3.16 * 10^{-6})^2/(3.3 * 10^{-7}) + 3.16*10^{-6} = 3.35 * 10^{-5}$ M
Moles = molarity * volume = $3.35 * 10^{-5} * 2 = 6.7 * 10^{-5}$ mol .
** Na^+ don't react at all because it's a conjugate acid of strong base **

Question : A 0.1 M solution of (CH_3NH_2) , contains $4.2 * 10^{-3}$ **OH^-** .
Calculate the % Ionization .

Answer : % ionization = $[OH^-]/[CH_3NH_2]_o$ *100% = 4.2 %

Question : find the pH of 0.02 M $CaCO_3$ solution . (K_b of $CO_3^{-2} = 1.8 * 10^{-4}$)

Answer : $CaCO_3$ is a salt→ gives CO_3^{-2}→ react as a weak base with water:

$CO_3^{-2} + H_2O \rightleftarrows HCO_3^- + OH^-$

now we check whether to neglect X or not :

$[CaCO_3]_o/K_b = 0.02/(1.8*10^{-4}) = 111.1 < 380$ → don't neglect

find $F = \sqrt{0.25 + [B]o/Kb} - 0.5 = 10$

→ $pH = 14 - pOH = 14 - (-\log FK_b) = 14 + \log(1.8*10^{-3}) = 11.25$

**** **the % Ionization decrease with the increase of $[B]_o$ & vise versa** .

Question : Rank the following according to their % of ionization :

1) 0.1 M CH_3NH_2 2) 0.1 M Na_2O 3) 0.01 M CH_3NH_2 4) 0.05 M CH_3NH_2

Answer : Na_2O is a strong base → 100% dissociation

CH_3NH_2 is a weak base : less concentration → higher ionization

so the ranking is : 2 > 3 > 4 > 1

Relative Strength of acids & bases

- The strength of acids (acidity) :

  strong acids > H_3O^+ > weak acids > H_2O > OH^- > H_2 ~ CH_4 ~ conj. Acids of strong bases (Li^+ , Na^+ , K^+ , Rb^+ , Ca^{+2} , Ba^{+2})

  regarding the weak acids themselves :

  the higher K_a , the stronger the acid (higher acidity & lower basicity) & the weaker the conjugate base .

- The strength of bases (basicity) :

  CH_3^- > strong bases (H^->O^{-2}> OH^-) > weak bases > H_2O > conj. bases of strong acids (Cl^- , Br^- , I^- , NO_3^- ,ClO_4^- , ClO_3^-)

  regarding the weak bases themselves :

  the higher K_b , the stronger the base (higher basicity & lower acidity) & the weaker the conjugate acid .

Question : Rank the following according to their basicity :

a) F^- b) NO_2^- c) Br^- d) CH_3COO^- e) H_2O f) OH^- .

(K_a of HF = $6.8*10^{-4}$),(K_a of HNO_2 = $4.5*10^{-4}$),(K_a of CH_3COOH = $1.8*10^{-5}$)

Answer : OH^- > weak bases (F^-,NO_2^-, CH_3COO^-) > H_2O > Br^-
now we compare the weak bases using the K_a of their acids :
higher K_a → weaker conjugate base : $F^- < NO_2^- < CH_3COO^-$
so the overall ranking is : **$OH^- > CH_3COO^- > NO_2^- > F^- > H_2O > Br^-$**

Question : Rank the following according to their acidity :
a) H_2S b) H_2O c) HCl d) HClO e) NH_4^+ f) H_3O^+ .
(K_b of HS^- = $1.8 * 10^{-7}$) , (K_b of ClO^- = $3.3 * 10^{-7}$) , (K_b of NH_3 = $1.8 * 10^{-5}$)
Answer : HCl (strong acid) > H_3O^+ > H_2S,HClO,NH_4^+ (weak acids) > H_2O
now we compare the weak acids using the K_b of their bases :
higher K_b → weaker conjugate acid : H_2S > HClO > NH_4^+ .
so the overall ranking is : **HCl > H_3O^+ > H_2S > HClO > NH_4^+ > H_2O**

(16.8) Relationship between K_a & K_b

For any acid-base reaction , there are 2 conjugate acid-base pairs , to correlate the strength of the acid & base in each pair , u can use this relationship :

$\boxed{K_a \text{ for conj. acid} = K_W / K_b \text{ of the base}}$ OR $\boxed{K_b \text{ for conj. base} = K_W / K_a \text{ of the acid}}$

which means that $\boxed{K_W = K_a * K_b} = 10^{-14}$ at 25 °C .
take (-log) → $\boxed{pK_W = pK_a + pK_b} = 14$ at 25 °C .

Let's take the following reaction at 25°C : $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$
K_b for NH_3 = $1.8 * 10^{-5}$, so :
K_a for the conjugate acid (NH_4^+) = $K_W/K_b = 10^{-14}/(1.8 *10^{-5}) = 5.56 *10^{-10}$

now we can write the reverse reaction as if it was the forward one :
$NH_4^+ + OH^- \leftrightarrows NH_3 + H_2O$ & the K_a for the acid (NH_4^+) = $5.56 *10^{-10}$
the nice thing is that **regardless of what reacts with NH_4^+ , the K_a & K_b are the same** : $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$ → K_a (NH_4^+) = $5.56 *10^{-10}$, K_b (NH_3) =$1.8 *10^{-5}$

(16.9) Acid-Base Properties of Salt Solutions

- U should save the strong acids & bases , then u should know that their conjugate acids or bases are very weak such that they can't react with anything , including water , which means they don't undergo hydrolysis in water . These conjugate acids & bases are :

conjugate acids of the strong bases : $\boxed{Li^+ , Na^+ , K^+ , Rb^+ , Ca^{+2} , Ba^{+2}}$.

conjugate bases of the strong acids : $\boxed{Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , ClO_3^-}$.

- Hydrolysis (تميّه) : reaction with water .

- The conjugate acids & bases of weak acids or bases have the ability to react , so they undergo hydrolysis & form either H_3O^+ or OH^- :

  $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$ → form acidic solution

  $ClO^- + H_2O \leftrightarrows HClO + OH^-$ → form basic solution

- The salts are 3 types : neutral , acidic , basic .
  - they are classified according to their effect in pH of water .
  - to determine whether the salt is neutral , acidic or basic , we just delete the conjugate acids & bases of strong bases & acids in the salt formula , then :
    1. if all the salt deleted → neutral salt .
    2. if we result in an anion –negative- which is a base according to lewis definition → the salt is basic .
    3. if we result in a cation –positive- which is an acid according to lewis definition → the salt is acidic .
    4. if nothing deleted from the salt (has no conjugate of strong acids & bases) → we look at the K_a & K_b given in the question :

       $K_a > K_b$ → acidic salt , $K_b > K_a$ → basic salt , $K_a = K_b$ → neutral .

Examples :

NaCl = $\cancel{Na}\cancel{Cl}$ ⇨ Neutral

KF = $\cancel{K}F^-$ ⇨ Basic

NH_4NO_3 = $NH_4^+\cancel{NO_3}$ ⇨ Acidic

CH_3COONH_4 = nothing deleted = compare K_a & K_b given

if $K_{b\,(CH_3COO^-)} > K_{a\,(NH_4^+)}$ OR $K_{b\,(NH_3)} > K_{a\,(CH_3COOH)}$ ⇨ Basic

if $K_{a\,(NH_4^+)} > K_{b\,(CH_3COO^-)}$ OR $K_{a\,(CH_3COOH)} > K_{b\,(NH_3)}$ ⇨ Acidic

if $K_{b\,(CH_3COO^-)} = K_{a\,(NH_4^+)}$ OR $K_{b\,(NH_3)} = K_{a\,(CH_3COOH)}$ ⇨ Neutral

Question : which of the following have a pH above 7 (→basic) :

$NaClO_3$, $(CH_3)_3NHI$, $FeCl_3$, **$Ba(ClO_2)_2$**

Answer : deleting : ----- →=7, $(CH_3)_3NH^+$→ acid , Fe^{+3} →acid , ClO_2^- → **base**

Question : which of the following have a pOH above 7 (→ acidic) :

$LiNO_3$, $RbCN$, **NH_4Br** , HCOOK

Answer : deleting : ------ → =7 , CN^- → base , NH_4^+ → **acid** , $HCOO^-$ → base

Question : what is the behavior of NH_4NO_2 , given that $K_a(HNO_2)= 4.5*10^{-4}$

$K_b(NH_3) = 1.8 * 10^{-5}$

1- Acidic . 2- Basic . 3- Neutral . 4- weak acid .

Answer : first of all it's a salt , so the 4th option is wrong , now we try to delete anything in the formula , nothing deleted → compare the K_a-K_b : $K_a > K_b$ → acidic effect (behavior) .

Special cases :

1- **HSO_4^-** anion is a **weak acid** & never be a base → acidic effect .
Example : $NaHSO_4$ → delete Na → HSO_4^- → **acidic .**

2- The **Amphiprotic** anion (anions with H^+ able to be donated) are not always bases , they may give acidic or basic effect based on its K_a or K_b . we write the two equations of the Amphiprotic anion (one as acid & the other as base) & we compare the K_a for it in the acidic equation & the K_b for it in the basic equation , the higher (K_a or K_b) makes its equation happen .

now u may say : "how can I recognize the amphiprotic anions?" , it's easy , the question when it gives u a salt having amphiprotic anion , it will always give u two or three K_a (K_{a1} , K_{a2} ,K_{a3}) for the polyprotic acid (in the net example it's $H_2C_2O_4$) , u immediately should know that there is an amphiprotic anion in the given salt , then u should write the equations of the amphiprotic & correlate each K_a with its equation .

the next example will clear everything for you :

Example : what is the effect of $NaHC_2O_4$ solution in water ?

(given that K_{a1} for $H_2C_2O_4 = 5.9 * 10^{-2}$, $K_{a2} = 6.4 * 10^{-5}$)

Answer :

$NaHC_2O_4$ → delete Na → $HC_2O_4^-$ (amphiprotic)→ write equations :

as acid : $HC_2O_4^- + H_2O \leftrightarrows C_2O_4^{-2} + H_3O^+$

as base: $HC_2O_4^- + H_2O \leftrightarrows H_2C_2O_4 + OH^-$

K_{a1} is for the first dissociation of $H_2C_2O_4$ → ($H_2C_2O_4 \leftrightarrows HC_2O_4^-$)

K_{a2} is for the second dissociation→ ($HC_2O_4^- \leftrightarrows C_2O_4^{-2}$)

so u correlate the K_{a1} with this equation

but this K_{a1} is for the conjugate acid

→ K_b for the base ($HC_2O_4^-$) = $K_W/K_{a1} = 10^{-14}/(5.9*10^{-2})= 1.7*10^{-13}$

while the K_{a2} are for this equation

Now we compare which is higher , K_{a2} or K_b ? → It's K_{a2} so the equation which will happen is the equation of $HC_2O_4^-$ as acid (the first one)

→ **<u>the effect of salt is acidic .</u>**

Question : what is the behavior of (K_2HPO_4) , given that :

$K_{a1} = 7.5 * 10^{-3}$, $K_{a2} = 6.8 * 10^{-8}$, $K_{a3} = 4.2 * 10^{-13}$

1- acidic 2- basic 3- neutral 4- can't be determined

Answer : delete K → HPO_4^{-2} → amphiprotic → equations :

as base : $HPO_4^{-2} + H_2O \leftrightarrows H_2PO_4^- + OH^-$ $K_b = K_W/\mathbf{K_{a2}}$ =→=$1.5*10^{-7}$

as acid : $HPO_4^{-2} + H_2O \leftrightarrows PO_4^{-3} + H_3O^+$ $K_a = \mathbf{K_{a3}} = 4.2 * 10^{-13}$

$K_b > K_a$ → the equation is the one as base → **<u>the salt is basic .</u>**

** **Rule** : To quickly determine which K_a is for an equation , look at the **highest negative charge in the equation**, then use the K_a which has the same number of this negative charge , take the previous equation :

$HPO_4^{-2} + H_2O \leftrightarrows H_2PO_4^- + OH^-$, the highest -ve charge = -2 → use K_{a2}

Calculating the exact pH or pOH for an acidic or basic salt

- Calculate the pH of a 0.10 M NaCN solution . K_a (HCN) = $4.9 * 10^{-10}$.

  Answer : firstly NaCN → $Na^+ + CN^-$,,, delete Na^+ ,,, CN^- react with water :

  $CN^- + H_2O \leftrightarrows HCN + OH^-$ $K_b = K_W/K_a = 10^{-14}/(4.9 * 10^{-10})= 2*10^{-5}$

then solve as always (weak base) → check if neglect x or not :
$[CN^-]/K_b = 0.1/(2*10^{-10}) = 4900 > 380$ → neglect x :
$[OH^-] = \sqrt{Kb * [CN^-]o} = \sqrt{2 * 10^{-5} * 0.1} = 1.4 * 10^{-3}$
pH = 14 – pOH = 14 – (- log [OH]) = 14 + log $(1.4 * 10^{-3}) = 11.15$

*note : $[CN^-] = [NaCN]$ because it's a salt & dissociate completely ,
actually if CN^- in the salt was 2 like $Ba(CN)_2$ then → $[CN^-] = 2 [Ba(CN)_2]$

- Calculate the pOH of a 0.5 M NH_4ClO_4 solution . $K_b (NH_3) = 1.8 * 10^{-5}$
  Answer : $NH_4ClO_4 \rightarrow NH_4^+ + ClO_4^-$,,, delete ClO_4^- ,,, NH_4^+ react with water :
  $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$, $K_a = K_W/K_b = 5.55 * 10^{-10}$
  (weak acid) → check whether neglect x or not :
  $[NH_4^+]/K_a = 0.5/(5.55 * 10^{-10}) >>> 380$ → neglect x :
  $[H_3O^+] = \sqrt{Ka * [NH4^{\mp}]o} = 1.66 * 10^{-5}$
  pOH = 14 – pH = 14 – (-log $[H_3O^+]$) = 9.22

Calculating pH & [polyprotic weak acid] in basic salt

- **Rule** : **For a salt having (-2) anion** that react with water & produce (-1) anion that also react with water to give a polyprotic weak acid :
  If **$K_{b1}/K_{b2} > 1000$** , then :
  1- $\boxed{[OH^-]_{total} = [OH^-]_1}$ **2-** $\boxed{[\text{polyprotic acid-}H_2A\text{-}] = K_{b2}}$

- **For a salt has (-3) anion :**
  If $K_{b1}/K_{b2} > 1000$, then **:**
  1- $\boxed{[OH^-]_{total} = [OH^-]_1}$ **2-** $\boxed{[H_2A^-] = K_{b2}}$
  If $K_{b2}/K_{b3} > 1000$, then :
  $\boxed{[\text{polyprotic acid-}H_3A\text{-}] = K_{b3}}$

  - We calculate $[OH^-]_1$ as normal weak base calculations :
    firstly we check to neglect x or not , then use the law we want .

- Examples :

- Calculate the $[H^+]$ in 1.0 M Rb_2CO_3 solution . given that :
  K_{a1} for $H_2CO_3 = 4.3 * 10^{-7}$, $K_{a2} = 5.6 * 10^{-11}$.

Answer :

$Rb_2CO_3 \rightarrow 2Rb^+ + CO_3^{-2}$,,, delete Rb ,,, CO_3^{-2} react with water :

$CO_3^{-2} + H_2O \leftrightarrows HCO_3^- + OH^-$, highest –ve = -2 → $K_{b1} = K_W/\underline{\mathbf{K_{a2}}} = 1.8*10^{-4}$

$HCO_3^- + H_2O \leftrightarrows H_2CO_3 + OH^-$, $K_{b2} = K_W/K_{a1} = 10^{-14}/(4.3*10^{-7}) = 2.3*10^{-8}$

now we check if this reaction give a considerable $[OH^-]$ or negligible :

$K_{b1}/K_{b2} = 1.8*10^{-4}/2.3*10^{-8} = 7.8*10^3$ $\underline{\mathbf{> 1000}}$ → $[OH^-]_{total} = [OH^-]_1$

check if neglect x or not : $[CO_3^{-2}]/K_b = 1/(1.8*10^{-4}) >> 380$ → neglect x

$[OH^-] = \sqrt{Kb * [CO3^{-2}]o} = \sqrt{1.8 * 10^{-4} * 1} = 0.0134$

$[H^+] = K_W/[OH^-] = 7.5 * 10^{-13}$

- Calculate $[H_2CO_3]$ in the previous solution .

  Answer : $K_{b1}/K_{b2} > 1000 \rightarrow [H_2CO_3] = K_{b2} = 2.3*10^{-8}$

- Calculate pH & $[H_3PO_4]$ in 0.5 M $Ca_3(PO_4)_2$ solution . given that :

  K_{a1} for $H_3PO_4 = 7.5 * 10^{-3}$ $K_{a2} = 6.2 * 10^{-8}$ $K_{a3} = 4.2 * 10^{-13}$

  Answer : delete Ca to get → PO_4^{-3} which react with water :

  $PO_4^{-3} + H_2O \leftrightarrows HPO_4^{-2} + OH^-$, $K_{b1} = K_W/K_{a3} = 2.4 * 10^{-2}$

  $HPO_4^{-2} + H_2O \leftrightarrows H_2PO_4^- + OH^-$, $K_{b2} = K_W/K_{a2} = 1.6 * 10^{-7}$

  $H_2PO_4^- + H_2O \leftrightarrows H_3PO_4 + OH^-$, $K_{b3} = K_W/K_{a1} = 1.33 * 10^{-12}$

  $K_{b1}/K_{b2} >> 1000 \rightarrow [OH^-]_{total} = [OH^-]_1$, check if neglect X or not :

  find $[PO_4^{-3}]$ firstly → $Ca_3(PO_4)_2 \rightarrow 3Ca^{+2} + \underline{\mathbf{2}}PO_4^{-3}$

  means that $[PO_4^{-3}] = 2*[Ca_3(PO_4)_2] = 2*0.5 = 1$ M (very important)

  then $[PO_4^{-3}]/K_{b1} = 41.6 < 380$:

  consider x → $[OH^-]_1 = FK_{b1} = 6*2.4*10^{-2} = 0.144$ (F= $\sqrt{.25 + 41.6}$ -.5 =6)

  → pH = 14 – pOH = 14 – (-log 0.144) = 13.16

  $[H_3PO_4] = K_{b3} = 1.33 * 10^{-12}$ because $K_{b2}/K_{b3} >> 1000$.

(16.11) Lewis Acids & Bases

$\mathbf{H^+ + :NH_3 \rightarrow NH_4^+}$

$\mathbf{Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+}$

$\mathbf{Cd^{+2} + 4I^- \rightarrow CdI_4^{-2}}$

$\mathbf{Fe^{+3} + 6CN^- \leftrightarrows [Fe(CN)]^{-3}}$

$\boxed{\mathbf{CO_2 + H_2O \leftrightarrows H_2CO_3}}$

$\boxed{\mathbf{H_3N: + BF_3 \rightarrow H_3N \rightarrow BF_3}}$

Lewis Base : electrons donor

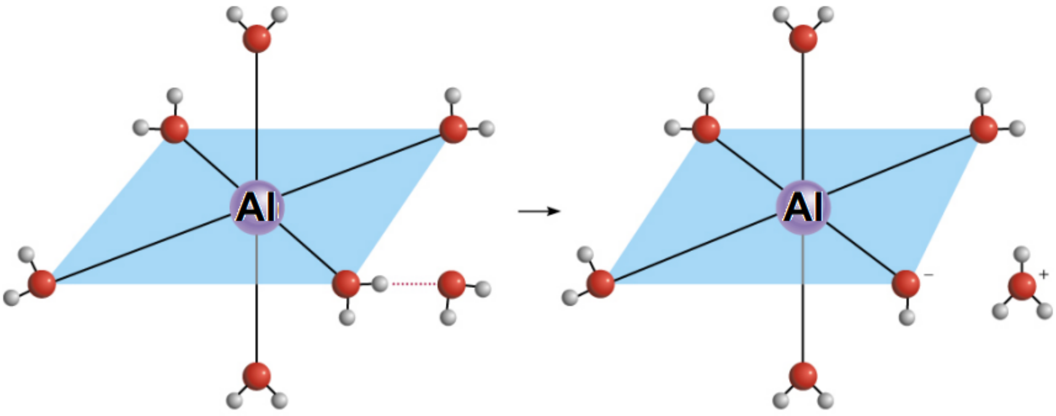
Lewis Acid : electrons acceptor

<u>notice the CO_2 being Lewis acid</u>

If u go back before this section , u can notice that we didn't mention how $FeBr_3$, $AlCl_3$, $Zn(NO_3)_2$, MgI_2 are acidic salts , we didn't put their exact reactions , we just said that we delete Br/I/Cl/NO_3 ,,, & the resultant positive ion is acidic so the salt has acidic behavior .

Lewis definition helps illustrate how these positive ions (Fe^{+3} , Zn^{+2} & Mg^{+2}) behave as acids . When the salt solve in water for example , these ions are freed, & their positive charges (empty orbital) attract the nonbonding pair of electrons in H_2O , so a Lewis acid-base reaction occurs , as a result of it , a water molecule loose one proton , generating the acidity .
Look at the Al^{+3} interaction with water molecules below & how one H_2O molecule (reacted with Al) loses a proton to a separate H_2O generating H_3O^+ .

$$6H_2\ddot{O}: + Al^{3+} \rightarrow Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$$



The reaction of the metal ion with water is called hydration , the $Al(H_2O)_6^{+3}$ can be written as $Al^{+3}(aq)$ & it has a K_a like other weak acids .

Another reaction with the exact same mechanism :
$Fe^{+3} + 6H_2O \rightarrow Fe(H_2O)_6^{+3} + H_2O \leftrightarrows Fe(H_2O)_5(OH^-)^{+2} + H_3O^+$
the acid is Fe^{+3} & the base is H_2O , K_a for $Fe^{+3}(aq) = 2*10^{-3}$ (just like weak acids)

In General : **the more charge** → more attraction → higher loss of protons
→ **higher acidity**
for the same charge → **smaller the ion higher the acidity** .

Question : which of the following has the lowest pH at the same concentration
1- $NaNO_3$ 2- $Ca(NO_3)_2$ 3- $Zn(NO_3)_2$ 4- $Al(NO_3)_3$

Answer : after deleting → $NaNO_3$ & $Ca(NO_3)_2$ are neutral (pH=7)
$Zn(NO_3)_2$ & $Al(NO_3)_3$ are acidic (Zn^{+2} , Al^{+3})
Al^{+3} higher charge → higher acidity → $Al(NO_3)_3$ has the lowest pH

End of Chapter 16

A question with an idea which I had in the final of my year :

- Calculate the pOH for 0.1 M HCl at 30 ^oC , $K_W = 5 * 10^{-14}$.
  Answer : $[H_3O^+] = [HCl] = 0.1$, $[OH^-] = K_W/[H_3O^+] = 5 * 10^{-14}/0.1$ & continue .
  ** this idea maybe given in weak acids/bases as well , so always remember that K_W is 10^{-14} only at 25°C , and if u are given at other temperatures , nothing will change except u will have a new value for K_W (for example) . :D

End of Chapter 16

(Chapter 17) (17.1) The Common-Ion Effect

- **Definition**: it's the shift in equilibrium caused by the addition of a strong electrolyte having an ion in common with a dissolved weak acid/base in the solution. **In other words** :
  if we have HOCl solution for example & we add to it a salt having a common Ion with it (OCl^-) or we add a strong acid (so common ion is H^+) then the equilibrium of the HOCl dissociation equation will be altered due to the added common ion , this alteration is called (Common ion effect) .

  Let's translate this into numbers & illustrate more :

  $$HOCl + H_2O \leftrightarrows H_3O^+ + OCl^-$$

  Initial conc. : 0.1 0 0 (suppose $[HOCl]_o$=0.1)
  at equilibrium : 0.1–X X X

  if we add a common ion , all the numbers in the previous equation will be altered , the common ion concentration will be increased , the other ion in the equation will be decreased & the acid conc will be increased , this is because some of the common ion after addition will react in **backward direction** , decreasing the other ion conc & increasing the acid conc , so X after addition of common ion will be decreased . (so $[HOCl]_{eq}$ is increased) if we add NaOCl (have OCl^- common with the previous acid) then equation becomes : $HOCl + H_2O \leftrightharpoons H_3O^+ + OCl^-$

at equilibrium : 0.1–X X [NaOCl]+X

if we add HCl (have H^+ common with the acid) then it becomes :

$HOCl + H_2O \leftrightharpoons H_3O^+ + OCl^-$

at equilibrium : 0.1–X [HCl]+X X

- in both of the previous additions , the X at equilibrium is lower than the X of the acid solution alone .

- The same thing occurs with a weak base , if u add a salt or a strong base having a common ion, the reaction goes in backward direction (**suppress the reaction**) .

- If the added substance have multiples of the common ion , then the concentration of the common ion added is the i*[added subs] :
  if we add $Ca(OCl)_2$ to the previous acid , then :
  $[OCl^-]$ at equilibrium = $2[Ca(OCl)_2] + X$

- **Rule :** for a mixed weak acid/base with its conjugate base/acid (salt) :
  1) always neglect X → $[conj]_{eq}$ = [common ion] in the mixed salt
  2) $[H_3O^+] = K_a * [acid]_{eq} / [conj]_{eq}$ for weak acid mixed with its salt
  $[OH^-] = K_b * [base]_{eq} / [conj]_{eq}$ for weak base mixed with its salt

  3) pH = pKa + log [conj]/[acid] for weak acid mixed with salt of conj
  pOH = pKb + log [conj]/[base] for weak base mixed with salt of conj
  these two are the two forms of Handerson-Hasselbalch equation

- **Rule :** for a mixed weak acid/base with a strong acid/base :
  1) always neglect X → $[H_3O^+]_{eq} = [H_3O^+]$ from the strong acid
  $[OH^-]_{eq} = [OH^-]$ from the strong base
  2) [conjugate] is calculated from the law of K_a or K_b , for example :
  $K_a = [H_3O^+]_{eq} * [conj]_{eq} / [acid]_{eq}$ → $[conj]_{eq} = K_a * [acid]_{eq} / [H_3O^+]_{eq}$

- **Examples :**
  - Calculate the $[H^+]$ in 0.1 M HOCl solution ($K_a = 3.0 \times 10^{-8}$) alone & in a mixed solution with 0.1 M NaOCl .

    Answer :

    alone → check if neglect x or not → >>380 → neglect →

    $[H_3O^+] = 5.5 \times 10^{-5}$ M

    mixed → $[OCl^-]_{eq} = [OCl^-]$ from NaOCl = [NaOCl] = 0.1 M

    the equation becomes : $HOCl + H_2O \leftrightarrows H_3O^+ + OCl^-$

    at equilibrium (after neglecting X) : 0.1 X 0.1

    $K_a = [H_3O^+]*[OCl^-]/[HOCl]_{eq} \rightarrow [H_3O^+] = K_a*[HOCl]_{eq}/[OCl^-]$

    $= 3.0 \times 10^{-8}$ M

    notice how X ($[H_3O^+]$) is decreased by the addition , means that the presence of the common ion suppressed the ionization of HOCl .

  - Calculate the pH and $[OCl^-]$ in a 0.20 M HOCl and 0.10 M HCl solution.

    Answer : common ion here is H^+ , $[H^+]_{eq} = [H^+]$ from HCl = [HCl] = 0.1

    the equation : $HOCl + H_2O \leftrightarrows H_3O^+ + OCl^-$

    at equilibrium (after neglecting X): 0.2 0.1 X

    $pH = - \log [H_3O^+] = - \log 0.1 = 1$

    $K_a = [H_3O^+]*[OCl^-]/[HOCl]_{eq} \rightarrow [OCl^-] = K_a*[HOCl]_{eq}/[H_3O^+]$

    $\rightarrow [OCl^-] = 6.0 \times 10^{-8}$ M

  - Calculate pH for a solution made by mixing 0.1 mol NH_3 & 0.1 mol NH_4Cl in 1 liter solution . (Kb for $NH_3 = 1.8 * 10^{-5}$)

    Answer : $pOH = pKb + \log [NH_4^+]/[NH_3]$ →→ pOH = 4.74 → pH = 9.26

(17.2) The Buffered Solutions

If u have a weak acid/base mixed with strong electrolyte that gives a common ion of its conjugate base/acid , then u have a **Buffered solution** in which its pH won't change much with small amounts of strong acid/base (resist the change).

- So the Buffer is either a weak acid + its conjugate base (HA/A^-)

  or a weak base + its conjugate acid (B/BH^+) .

Question: which of the following isn't a Buffer:
a) CH_3COOH/CH_3COO^- b) NH_3/NH_4^+ c) HPO_4^{-2}/ PO_4^{-3} d) HCl/Cl^-
Answer: d (strong acid/conj) , notice that c is weak acid/conj

- So the Buffer resist the change upon adding small amounts of strong acid/base , while the normal weak acid/base will change drastically .
  But How ?
  in the equation of the Buffer we have 2 things , an acid at one side & a base at the other , so if u add a strong acid , the H^+ given will not acidify the solution because they will react with the base of the Buffer resulting in increase in the acid of the buffer , while when u add a strong base , the OH^- produced will not remain as they are –basicity- but they will react with the acid of the buffer resulting in increase in the base of the Buffer .

- As a Conclusion :
  adding strong acid to Buffer → increase [acid] & decrease [base] by the same concentration of [H^+] in the strong acid
  adding strong base to Buffer → increase [base] & decrease [acid] by the same concentration of [OH^-] produced by the strong base

- Let's take the HOCl mixed with NaOCl example from previous section :

$$HOCl + H_2O \leftrightarrows H_3O^+ + OCl^-$$

	HOCl	H_3O^+	OCl^-
at equilibrium (after neglecting x) :	0.1	X	0.1
if we add 0.02 M HBr then :	0.1+0.02	X	0.1-0.02

notice that HBr (acid) increased [HOCl] by 0.02 (the same of [H^+] in HBr) while decreased [OCl^-] by 0.02 ,,, and surely X after addition is different from X before (more because we added acid) , but the difference is slight comparing to addition of the same concentration to 0.1 HOCl solution .

Example : calculate the pH before & after the addition of the 0.02 HBr into A) 0.1 M HOCl solution . B) 0.1 M HOCl & 0.1 M NaOCl .
(given that K_a for HOCl = $3.0 * 10^{-8}$)

Answer :
A) before → we calculated it → [H_3O^+] = 5.5×10^{-5} M → pH = 4.26

after → $[H_3O^+]_{eq}$ = $[H_3O^+]$ from HBr = 0.02 → pH = 1.7

* the solution pH fell from **4.26 into 1.7** after adding only 0.02 HBr *

B) before → by Handerson equation → pH = pKa →→ pH = 7.5

after → $HOCl + H_2O \leftrightarrows H_3O^+ + OCl^-$

at eq (after neglect x & adding HBr) : 0.1+0.02 X 0.1-0.02

0.12 X 0.08

→→ $[H_3O^+] = K_a * [HOCl]_{eq}/[OCl^-] = 4.5 * 10^{-8}$ → pH = 7.35

* look how the Buffer resist the change , pH changed only by 0.15 *

Buffer Capacity

Definition : Amount of strong acid or strong base the buffer can neutralize without significant change in pH.

Every buffer can resist the changes in pH within a limit for sure , beyond that limit it will lose this resistant & will start to change much , this is the buffer capacity , when the pH of the buffer is 1 unit around its pKa , the buffer will do its function , more than 1 unit around pKa → no buffering .

So Buffer Capacity is within **pH of 1 ± pKa =** the usable range of the buffer

- **The more concentrations of Buffer → more resistant to changes → better the buffer , but these concentrations must be equal , the more equal concentrations of the buffer → the more pH closer to pKa (according to Handerson eq) → the better buffer capacity .**

  Example : which is the best buffer **:**

  a) 1 M CH_3CO_2H / 1 M $CH_3CO_2^-$ b) 0.1 M CH_3CO_2H /0.1 $CH_3CO_2^-$

  c) 1.5 M CH_3CO_2H / 0.5 M $CH_3CO_2^-$ d) 2 M HCl / 2 M Cl^-

  Answer : a (because it has equal concentrations & higher than in b)

  d is not a buffer .

- More examples on buffers :
  - Calculate the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK . given that : Ka = 1.7×10^{-4} , pKa = 3.77

Answer : use handerson equation →→ pH = 4.01

- In the previous question , calculate pH after the addition of 0.10 mol HCl gas to 1.0 L of solution .

  Answer : $HCOOH + H_2O \leftrightarrows HCOO^- + H_3O^+$

  conc : 0.3+0.1 0.52-0.1 X

  so pH = pKa + log [HCOOH]/[$HCOO^-$] = 3.77 + log 0.4/0.42

  → pH = 3.79

- Calculate the pH of a 0.30 M NH_3/0.36 M NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 M NaOH to 80.0 mL of the buffer solution?

  (given that pKa for NH_4^+ = 9.25) (→ pKb = 14-pKa = 4.75)

  Answer : equation : $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

  concentrations before adding : 0.3 0.36 X

  the added [NaOH] = mass(solute)/V(soln)

  = MV(solute)/V(soln) =0.05*20/80= 0.0125

  so the conc after adding : .3+.0125 .36-.0125 X

  pOH = pKb + log [NH^+]/[NH_3] →→ pOH = 4.8 → pH = 9.2

- Calculate the concentration of sodium benzoate that must be present in a 0.20 M solution of benzoic acid to produce pH of 4.00 . (given that Ka = 6.5×10^{-5}) .

  Answer : using handerson eq → pH = pKa + log [salt]/[acid]

  → 4 = (-log 6.5×10^{-5}) + log [salt]/0.2

  → 4 = 4.19 + log [salt]/0.2 → log [salt]/0.2 = - 0.19

  log [salt] – log 0.2 = - 0.19 → log [salt] = - 0.886

  (shift+log+ -0.886) → [salt] = 0.13

- Calculate the pH of a solution formed by mixing 55 mL of 0.20 M $NaHCO_3$ with 65 mL of 0.15 M Na_2CO_3 .

  (given that pKa_1 for H_2CO_3 = 3.6 , pKa_2 = 10.25)

  Answer : this is a very clever & important question , u have two salts that when solve together will give two ions of the same polyprotic acid , they will form a Buffer which has a pH . look :

$NaHCO_3 \rightarrow Na^+ + HCO_3^-$ $Na_2CO_3 \rightarrow 2Na + CO_3^{-2}$

together → $HCO_3^- + H_2O \leftrightarrows CO_3^{-2} + H_3O^+$

$[HCO_3^-] = [NaHCO_3] = MV/V_{total} = 0.2*55/120 = 0.092$

$[CO_3^{-2}] = [Na_2CO_3] = MV/V_{total} = 0.15*65/120 = 0.081$

so the concentrations : 0.092 0.081 X

→ handerson equation → pH = 10.2

How to Prepare a Buffer

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pH = pKa + log [A-]/[HA]

here we are going to learn how to make the best buffer for a specified pH value , the first thing is to choose a weak acid whose pKa close to required pH (the more close the more effective) , then calculate [A-]/[HA] ratio that is required to adjust to the required pH value , this is done through applying pH & pKa to Handerson eq. , after we know the [A-]/[HA] ratio we should prepare a real weak acid (HA) with its conjugate base (A^-) solution with the calculated ratio , this is done through :

1- Mixing available HA & A^- with a calculated quantities

2- If we don't have a salt for the weak acid (the conjugate) , then we can add some strong base to the weak acid , this will generate a conjugate base with the same concentration of the reacted strong base : $\mathbf{HA + OH^- \rightarrow H_2O + A^-}$

initial conc (for example) : 0.5 0.2 0

0.2 M HA will react completely with 0.2 M OH^- to produce 0.2M A^-

equilibrium conc : 0.3 0 0.2

3- If we don't have a weak acid but have the salt (conjugate) , then we can add some strong acid to the conjugate base to form the weak acid : $A^- + H^+$ (from st acid) → HA

Examples :

- H_3A is a polyprotic acid with ($Ka_1=10^{-3}$, $Ka_2=10^{-6}$, $Ka_3=10^{-11}$)**.** which one of the following solutions would you use to prepare a buffer with pH = 6 ?

a) 0.1 M H_3A , 0.1 M H_2A^- b) 0.1 M H_2A^- , 0.1 M HA^{-2}
c) 0.1 M HA^{-2} , 0.1 M A^{-3} d) 0.1 M H_3A , 0.1 A^{-2}

Answer : firstly d is not a buffer , secondly the needed buffer has a pKa = pH = 6 , so we need the equation of Ka_2 (highest –ve charge = -2) → b

- How many moles of NH_4Cl must be added to 2 L of 0.1 M NH_3 to form a buffer whose pH = 9 ? (Kb for NH_3 = $1.8*10^{-5}$) .

  Answer : use handersun equation :

  pOH = pKb + log $[NH_4^+]/[NH_3]$

  →5 = 4.74 + log n(NH_4^+)/2/0.1 → log n(NH_4^+) = 0.26+log 0.2

  → log n = -0.44 → n = 0.36 moles

End Of Chapter 17

Finished :D

Hope the best for u All , study hard & u will do it

Sorry for any mistake

ادعولي يا جماعة ترى والله ملحوق كثير بدراستي
:P

And As always , sorry for the long summary , ur material is quite long , be patient & ﷲ will help u

Take Care

your brother