1、Acid and base theorem

Arrhenius Theorem

Bronsted&Lowry Theorem   (Proton)

Lewis acid and base Theorem   (Electron)

Hard Soft Acid and base

2、Bronsted&Lowry Theorem

Acid: Proton Donor

Base:Proton Acceptor
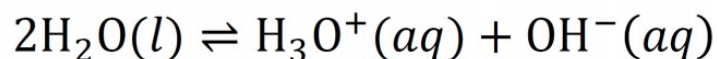
Strong acid base: complete······

Weak acid base: Partly······

Conjugate acid and base pair:

Acid=H$^+$+base for example: HAc , Ac$^-$ is one pair of conjugate acid and base

3、Water

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- Recall the equilibrium constant:
$$K_W = [H_3O^+][OH^-]$$

- At 25°C, in pure water
$$[H_3O^+] = 1 \times 10^{-7}; [OH^-] = 1 \times 10^{-7}$$
$$K_W = 1 \times 10^{-14}$$

- Remember that K_W is only related to T
  - So at certain temperature, the product of $[H_3O^+]$ and $[OH^-]$ in a solution is constant.
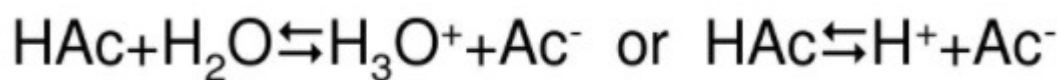
$$pH = -\log_{10}[H_3O^+]$$

Similarly,

$$pOH = -\log_{10}[OH^-]$$

In a solution at 25°C,

$$pH + pOH = 14$$

4、The equiliburim problem about Monobasic weak acid
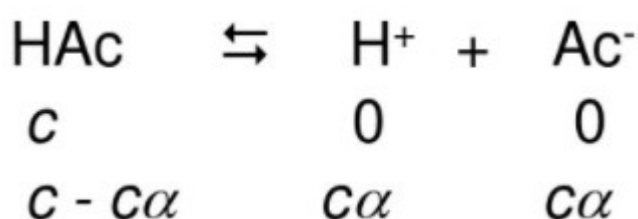
$$HAc+H_2O \leftrightarrows H_3O^+ + Ac^- \quad \text{or} \quad HAc \leftrightarrows H^+ + Ac^-$$

At a certain tempreture, there exist the equiliburim constant Ka

$$K_a = [H^+][Ac^-]/[HAc]$$

Disassociation degree α , which is a constant describing the extent of ionization

$$\alpha = (\text{已电离的浓度}/\text{弱电解质的初始浓度}) \times 100\%$$

Consider a problem of the ionization equiliburim of 0.1M HAc

$$
\begin{array}{cccc}
HAc & \leftrightarrows & H^+ & + & Ac^- \\
c & & 0 & & 0 \\
c - c\alpha & & c\alpha & & c\alpha
\end{array}
$$

$$K_a = c\alpha^2/(1-\alpha)$$

Applying the 5% approximation:

If $\alpha \leq 5\%$, which shows that c/Ka>=400, 1- α =1,we can derive the formula that:

$[H^+]=\sqrt{Ka*c}$ Which is a very useful and simple formula.

Thinking about the discussion above, is there any problem?

Yes! We have ignore the ionization of water automatically, which is not good. But in this case, we can, why? Because the extent of the ionization of water is too weak compare to the ionization of HAc. So, how weak is weak?

Apply 5% approximation too, the precise calculation should be $[H+]=(Ka[HA]+Kw)^{0.5}$ so

when Kw<=5%Ka*c, we can ignore the effect of water ionization:

Which shows us that Ka*c>=20Kw.

All in all, when the two condition:

Ka*c>=20kw; c/ka>=400 are satisfied we can using the formula $[H^+]=\sqrt{Ka*c}$ to calculate the PH.

Then if c/ka>=400 but Ka*c<20kw, we can not ignore the ionization of water so we must apply the

formula $[H+]=(Ka[HA]+Kw)^{0.5}$

Then if Ka*c>=20kw but c/ka<400, we must solve the equation

$$HAc \leftrightarrows H^+ + Ac^-$$

$$0.10 \quad\quad 0 \quad 0$$

$$0.10-x \quad\quad x \quad x$$
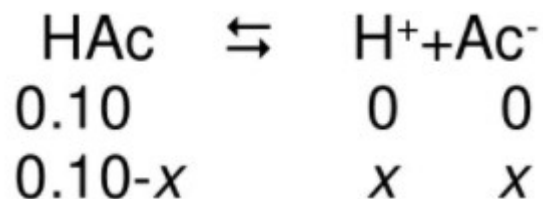
$$K_a = x^2/(0.10-x)$$

Solving for x and we can get PH

Finally, if neither of the 2 condition are satisfied, we shall apply the general solution:

$$K_a = \frac{[H_3O^+]\left([H_3O^+] - \dfrac{K_w}{[H_3O^+]}\right)}{[HA]_{initial} - [H_3O^+] + \dfrac{K_w}{[H_3O^+]}}$$

Constant table(Do not coppy it on your ctpp!)

酸	K_a	pK_a	碱	K_b	pK_b
HIO_3	1.69×10^{-1}	0.77	IO_3^-	5.1×10^{-14}	13.29
$H_2C_2O_4$	5.90×10^{-2}	1.23	$HC_2O_4^-$	1.69×10^{-13}	12.77
H_2SO_3	1.54×10^{-2}	1.81	HSO_3^-	6.49×10^{-13}	12.19
HSO_4^-	1.20×10^{-2}	1.92	SO_4^{2-}	8.33×10^{-13}	12.08
H_3PO_4	7.52×10^{-3}	2.12	$H_2PO_4^-$	1.33×10^{-12}	11.88
HNO_2	4.6×10^{-4}	3.37	NO_2^-	2.17×10^{-11}	10.66
HF	3.53×10^{-4}	3.45	F^-	2.83×10^{-11}	10.55
$HC_2O_4^-$	6.40×10^{-5}	4.19	$C_2O_4^{2-}$	1.56×10^{-10}	9.81
HAc	1.76×10^{-5}	4.76	Ac^-	5.68×10^{-10}	9.25
H_2CO_3	4.30×10^{-7}	6.37	HCO_3^-	2.32×10^{-8}	7.63
HSO_3^-	1.02×10^{-7}	6.91	SO_3^{2-}	9.8×10^{-8}	7.01
$H_2PO_4^-$	6.23×10^{-8}	7.21	HPO_4^{2-}	1.6×10^{-7}	6.8
H_2S	5.7×10^{-8}	7.24	HS^-	1.75×10^{-7}	6.76
$HClO$	2.95×10^{-8}	7.53	ClO^-	3.39×10^{-7}	6.47
NH_4^+	5.64×10^{-10}	9.25	NH_3	1.774×10^{-5}	4.751
HCN	4.93×10^{-10}	9.31	CN^-	2.03×10^{-5}	4.69
HCO_3^-	5.61×10^{-11}	10.25	CO_3^{2-}	1.78×10^{-4}	3.75
HPO_4^{2-}	2.2×10^{-13}	12.66	PO_4^{3-}	4.54×10^{-2}	1.34
HS^-	1.2×10^{-15}	14.92	S^{2-}	8.33	-0.92

Exercise:

1、 Calculate the PH of the 0.01M HAc solution at 25℃

2、 Calculate the PH of the 0.00001M HCN solution at 25℃

3、 Calculate the PH of the 1x10^(-8)M HCl solution at 25℃

4、 Problems about the Polyprotic Acid Consider the equiliburim of H2CO3

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$
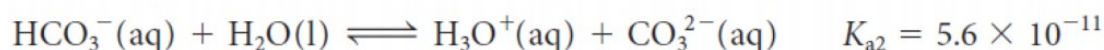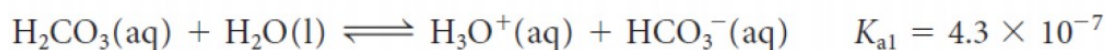
$$K_{a1} \gg K_{a2} \gg K_{a3} \gg \cdots$$

Reversibly,

$$K_{b1} = \frac{K_W}{K_{a1}} \ll K_{b2} = \frac{K_W}{K_{a2}} \ll K_{b3} = \frac{K_W}{K_{a3}} \ll \cdots$$
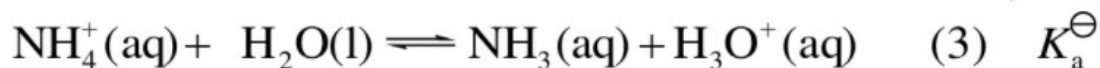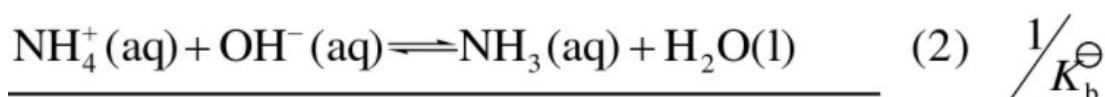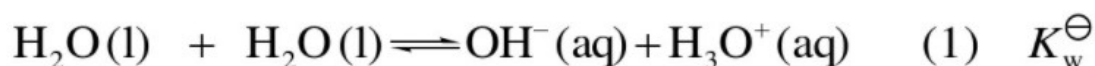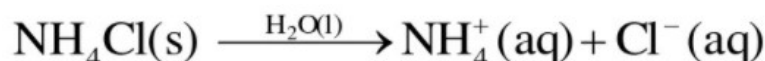
Tricks:

- Estimate the pH of a polyprotic acid for which all deprotonations are weak by using only the first deprotonation equilibrium and assuming that further deprotonation is insignificant.

Reason(5% approximation)

Exercise：Calculate the PH of a 0.01M H$_2$CO3 solution at 25℃, and derive the concentration of [OH$^-$],[HCO$_3^-$],[H$_2$CO$_3$],[CO$_3^{2-}$]

5、 Hydrolysis Equiliburim about Salt solution

<mark>partI:Strong acid weak base salt</mark>

$$NH_4Cl(s) \xrightarrow{\ H_2O(l)\ } NH_4^+(aq) + Cl^-(aq)$$

$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq) \qquad (1) \quad K_w^{\ominus}$$

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l) \qquad (2) \quad \dfrac{1}{K_b^{\ominus}}$$

$$\overline{\rule{0pt}{0pt}\hspace{11cm}}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad (3) \quad K_a^{\ominus}$$

(1) +(2)=(3)

$$K_a^{\ominus}(NH_4^+) = \frac{\{c(H_3O^+)\}\{c(NH_3)\}}{\{c(NH_4^+)\}} \cdot \frac{c(OH^-)}{c(OH^-)} = \frac{K_w^{\ominus}}{K_b^{\ominus}(NH_3)}$$

Exercise

Calculate the PH of 0.1M NH4Cl solution under 25℃

$$Ac^-(aq) + H_2O(l) \rightleftharpoons HAc(aq) + OH^-(aq)$$

$$K_b^{\ominus}(Ac^-) = \frac{\{c(HAc)\}\{c(OH^-)\}}{\{c(Ac^-)\}} = \frac{K_w^{\ominus}}{K_a^{\ominus}(HAc)}$$

The case of Salt of Polyprotic Acid

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$K_{b,1}^{\ominus}(CO_3^{2-}) = \frac{K_w^{\ominus}}{K_{a,2}^{\ominus}(H_2CO_3)} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$
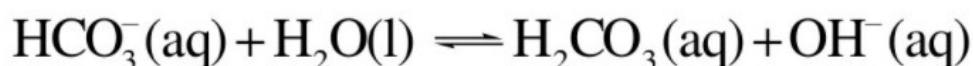
$$K_{b,2}^{\ominus}(CO_3^{2-}) = \frac{K_w^{\ominus}}{K_{a,1}^{\ominus}(H_2CO_3)} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8}$$

$$K_{a,1}^{\ominus}(H_2CO_3) \rangle\rangle K_{a,2}^{\ominus}(H_2CO_3), \quad K_{b,1}^{\ominus}(CO_3^{2-}) \rangle\rangle K_{b,2}^{\ominus}(CO_3^{2-})$$

$$NH_4Ac(s) \longrightarrow NH_4^+(aq) + Ac^-(aq)$$

$$NH_4^+(aq) + Ac^-(aq) + H_2O(l) \rightleftharpoons NH_3 \cdot H_2O(aq) + HAc(aq)$$
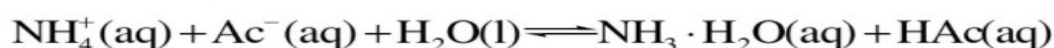
$$K_a^{\ominus} < K_b^{\ominus} \quad 碱性 \quad NH_4CN \quad K_a^{\ominus}(HCN) = 5.8 \times 10^{-10}$$
$$K_b^{\ominus}(NH_3 \cdot H_2O) = 1.8 \times 10^{-5}$$

$$K_a^{\ominus} = K_b^{\ominus} \quad 中性 \quad NH_4Ac \quad K_a^{\ominus}(HAc) = 1.8 \times 10^{-5}$$
$$K_b^{\ominus}(NH_3 \cdot H_2O) = 1.8 \times 10^{-5}$$

$$K_a^{\ominus} > K_b^{\ominus} \quad 酸性 \quad NH_4F \quad K_a^{\ominus}(HF) = 6.9 \times 10^{-4}$$
$$K_b^{\ominus}(NH_3 \cdot H_2O) = 1.8 \times 10^{-5}$$

Optional part(beyond CHEM2100J Genral Chemistry)
Acid and base equiliburim analyzing method in Analytic Chemistry(分析化学，化学系专业课）
Method of Distribution coefficient(Try to understand this,because it may be your strongest weapon in this chaper):
Consider the equiliburim of H_2CO_3, we can get:

$$\text{Let M} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

$$\text{(M is constant) Why?}$$

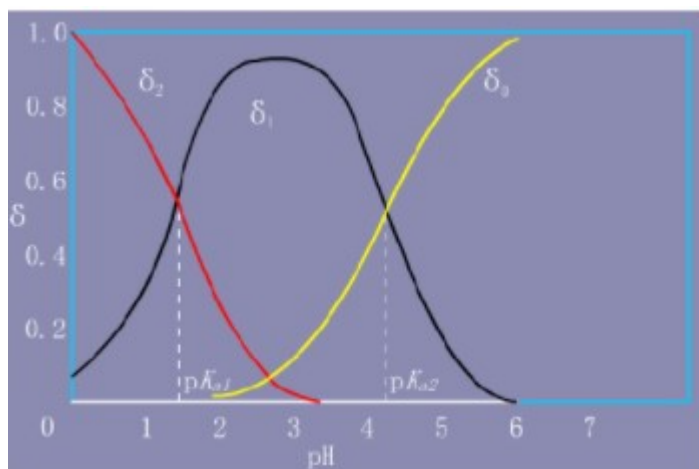$$\text{Let } X_0 = \frac{[H_2CO_3]}{M}, \, X_1 = \frac{[HCO_3^-]}{M}, \, X_2 = \frac{[CO_3^{2-}]}{M}$$

$$\text{Then we have:} \begin{cases} K_{a1}X_0 = [H_3O^+]X_1 \\ K_{a2}X_1 = [H_3O^+]X_2 \\ X_0 + X_1 + X_2 = 1 \end{cases} \text{Solve it.}$$

$$X_0 = \frac{[H_3O^+]^2}{[H_3O^+]^2 + [H_3O^+]k_{a1} + k_{a1}k_{a2}}$$

$$X_1 = \frac{[H_3O^+]k_{a1}}{[H_3O^+]^2 + [H_3O^+]k_{a1} + k_{a1}k_{a2}}$$

$$X_0 = \frac{k_{a1}k_{a2}}{[H_3O^+]^2 + [H_3O^+]k_{a1} + k_{a1}k_{a2}}$$

The final one should be X3, all of them are mole fraction.

Analyzing the formula above, what can we find: As long AS We Know the PH, we can solve everything about the solution.

Pay attention to the fact that we can also apply this method to NaHCO3,Na2CO3 solution because they all consists of the same ions execpt Na⁺, which will cause no effect!

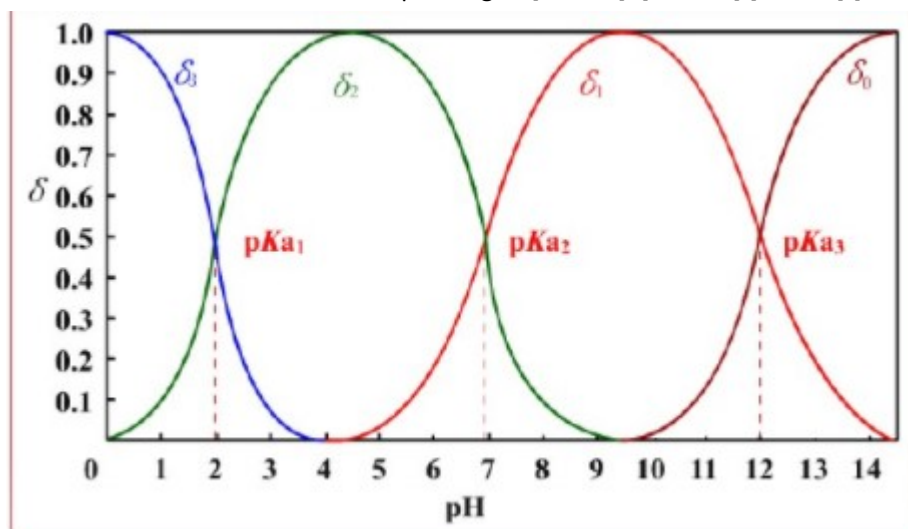We can also consider the case of more complex acid or base or salt, for example

H3PO4

$$\delta_3 = \frac{[H^+]^3}{[H^+]^3+[H^+]^2 K_{a_1}+[H^+]K_{a_1} \times K_{a2}+K_{a_1} \times K_{a2} \times K_{a3}}$$

$$\delta_2 = \frac{[H^+]^2 K_{a_1}}{[H^+]^3+[H^+]^2 K_{a_1}+[H^+]K_{a_1} \times K_{a2}+K_{a_1} \times K_{a2} \times K_{a3}}$$

$$\delta_1 = \frac{[H^+] K_{a_1} \times K_{a2}}{[H^+]^3+[H^+]^2 K_{a_1}+[H^+]K_{a_1} \times K_{a2}+K_{a_1} \times K_{a2} \times K_{a3}}$$

$$\delta_0 = \frac{K_{a_1} \times K_{a2} \times K_{a3}}{[H^+]^3+[H^+]^2 K_{a_1}+[H^+]K_{a_1} \times K_{a2}+K_{a_1} \times K_{a2} \times K_{a3}}$$

Which are the mole fraction corresponding to [H3PO4], [H2PO4-],[HPO4^{2-}],[PO4^{3-}].

We can also apply this method to any corresponding salt solution.

All in all, with the help of the method of Distribution coefficient we can solve anything as long as we know the PH.
So, when you meet a Polyprotic problem you can solve it using the following step
1、 Calculate the concentration of H$^+$ using Ka1
2、 Apply the Distribution Coefficient method, plug in numbers into the calculator
3、 Write down the answer can get full marks
Exercise： Calculate the PH of a 0.01M H$_2$CO3 solution at 25℃, and derive the concentration of [OH-],[HCO$_3$-],[H$_2$CO$_3$],[CO$_3{}^{2-}$] using the method of Distribution coefficient.

Reference:

VC210 2020FALL RC9, Shi Wei
General Chemistry Slides, Fudan University

Thank You for listening my last regular RC and Goodbye!

Linda Wei