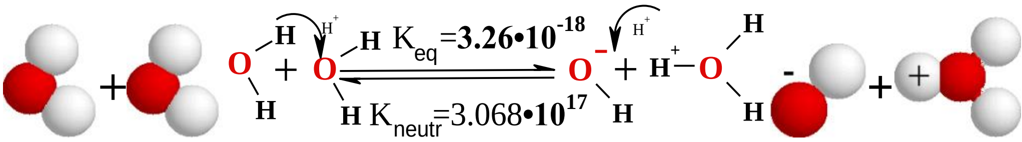
Āris Kaksis 2022, Riga Stradin's University

DISSOCIATION and WATER protolysis. pH exponent of hydrogen ion $[H_3O^+]=10^{-pH}$.

Brensted high rate water protolysis 1923 is thousand times faster. Therefore rapid reaction deprotonation protonation $H_2O+H_2O \Leftrightarrow H_3O^++HO^-$ is at equilibrium state, while other reactions mach slower continues as non-equilibrium state reactions. Protolysis high rate equilibrium state of deprotonation support the water concentration value $[H_2O]=55.3$ M as reactants $H_2O+H_2O \Leftrightarrow$ and homeostasis established attractor value pH=7,36 support the protolysis as negligible product amount $\Leftrightarrow H_3O^++HO^-$ hydroxonium ion and hydroxide ion concentrations $[H_3O^+]=10^{-7,36}$ M so $[HO^-]=10^{-6.64}$ M.

High rate protolysis weak acid H_2O cleaves the proton H^+ protonate second H_2O molecule, which turns to strong acid H_3O^+, and remains $OH^—$. Protolysis is thermodynamic correct is mol fractions equilibrium constant:



$$K_{eq}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3.26\cdot10^{-18}$$

Dissociated concentrations of **water** ions are smaller $[H_3O^+]=[OH^-]=10^{-7}$ M than H_2O concentration 55.3 M, which is in large excess at T=298.15 K. What can be calculate as 1 liter mass **m=996.68 g** divided by **water** molar mass M_{H_2O}**=18 g/mol**. Two molecule collisions for second order reaction exponent square power is concentration factorial : $[H_2O]\,[H_2O]=[H_2O]^2=3065.96$ M²; $[H_2O]=^{m}/M_{H_2O}=^{997}/18=$ **55.3** $^{mol}/$L.

Two times the **water** concentration exponent 2 with $K_{eq}*[H_2O]^2$ we have got the classic **water** constant K_w:

$$K_w = [H_3O^+]\cdot[OH^-] = 55{,}37^2\cdot3.26\cdot10^{-18}= 10^{-14} = 0.00000000000001$$

This last equation has usual application: $pK_w= -\log K_w=14$=pH+pOH for pH and pOH balance in constant **.**

It means, that in pure **water**, as well as in all **water** solutions the product of H_3O^+ and $OH^—$ concentrations is constant and it is 10^{-14}. This means, that none of these two concentrations can be changed alone. If, for example, an acid is added and $[H_3O^+]$ increased, $[OH^-]$ must decrease to maintain the product of concentrations constant $[H_3O^+]\cdot[OH^-] = K_w = 10^{-14}= 10^{-pKw}$ and $pK_w=14$=pH+pOH .

It also means that in pure **water** or any other neutral environment, which is equal acidic and equal basic, both concentrations of $[H^+]$ and $[OH^-]$ are equal and each of them can be calculated as **14** = pH + pOH:

$$[H_3O^+]=[OH^-]=\sqrt{K_w}=\sqrt{10^{-14}}=10^{-7}\ \frac{mol}{L}\ (M)=0.0000001\ \frac{mol}{L}\ (M)$$

Water protolysis increases free energy content for products $H_3O^++OH^—$ from zero 0 to $G_{H3O+OH}=99.8$ $^{kJ}/_{mol}$:

$H_2O+H_2O<=>H_3O^++OH^—$; $K_{eq}=[H_3O^+]*[OH^—]/[H_2O]^2=3.26\cdot10^{-18}$; $\Delta G_{eq}=-R\cdot T\cdot\ln(K_{eq})=99.8$ $^{kJ}/_{mol}$.

$\Delta G_{H3O++OH-}=-R\cdot T\cdot\ln(K_{H3O++OH-})=-8{,}3144*298{,}15*\ln(3{,}26\cdot10\text{^}(^{-18}))/1000=99.8$ $^{kJ}/_{mol}$.

$G_{H3O++OH-}=\Delta G_{H3O++OH-}+\Delta G°_{2H2O}=-R\cdot T\cdot\ln(K_{H3O++OH-})+2*0=99.8$ $^{kJ}/_{mol}$. [1,8,14]

Note: **Water** concentration is used classically constant $[H_2O]=55{,}3$ M. Therefore classic acid constant K_a is water concentration factorial with thermodynamic acid constant $K_a=K_{a\_H2O}*[H_2O]$:

$$K_a=K_{a\_H2O}*[H_2O]=^{1}/(K_{b\_H2O}*[H_2O])=^{1}/K_b;$$

Deprotonated acid **aH** create hydroxonium H_3O^+ and turns to base⁻: $aH + H_2O \Leftrightarrow H_3O^+ + b^-$

$$K_{a\_H2O}=\frac{[b^-]\cdot[H_3O^+]}{[aH]\cdot[H_2O]}\ ;\ K_{b\_H2O}=\frac{[aH^+]\cdot[OH^-]}{[b]\cdot[H_2O]}$$

H_2O protonated base create acid aH^+ and hydroxide OH^- ion: $b + H_2O \Leftrightarrow bH^+ + OH^-$.

If acid **aH** is weak deprotonate acid-base b^- is strong ; If base **b** is strong protonate base-acid bH^+ is weak.

Water is protolytic acid H_2O which cleaves the proton H^+ protonate second H_2O molecule, which is the base.

So in protolytic reaction forms the strong base hydroxide $OH^—$ ions and strong acid hydroxonium H_3O^+ ions.

Water weak acid and weak base but $OH^—$ strong base neutralizes with H_3O^+ strong acid forming practically non dissociated **water** molecules. Therefore protolysis equilibrium constant is small positive number $K_{eq}=3.26\cdot10^{-18}$.

1. David R. Lide. CRC Handbook of Chemistry and Physics .90th ed. Taylor and Francis Group LLC; 2010 .

8. Alberty RA. Biochemical Thermodynamic's : Applications of Mathematics. John Wiley & Sons, Inc. 1-463, (2006).

Scale of pH with the corresponding values of pOH and [H^+] in acidic and basic medium

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pOH	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
[H^+]	1	0.1	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
	acidic				*slightly acidic*			*neutral*	*slightly basic*			*alkaline*			

pH of human **blood** is **7.36** - slightly basic, because it must have a reserve of alkalinity to fight the acidic products of metabolism.

Values **0** and **14** at the ends of pH scale mean:

__pH__ = __0__ means a __1__ molar solution of H^+ ions (__1__ molar strong univalent acid),

__pH__ = __14__ means, that __pOH__ = __14 - pH__ = __0__ - it is a __1__ molar solution of a strong univalent base.

pH of some well-known liquids is given in figure **4.2**.

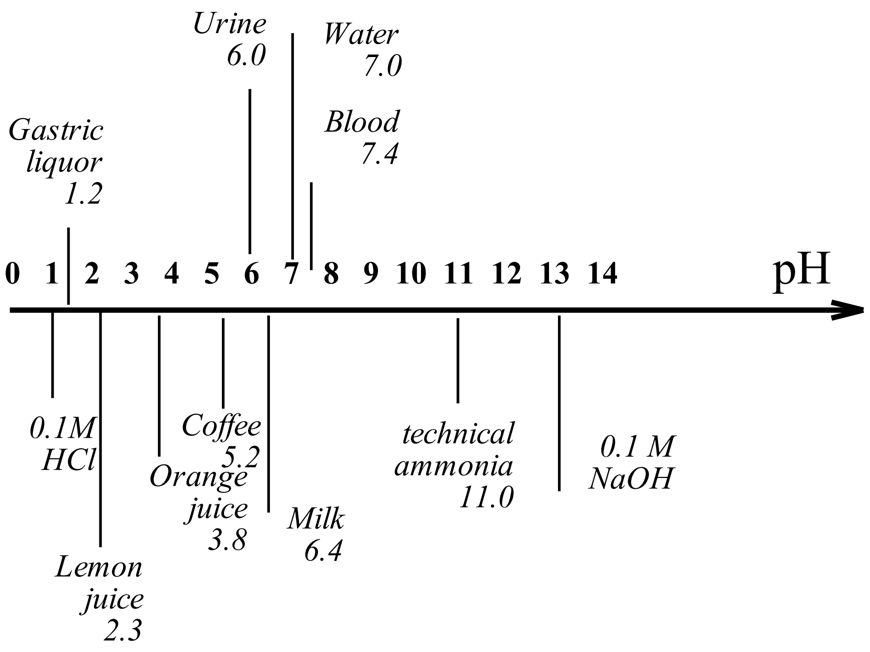
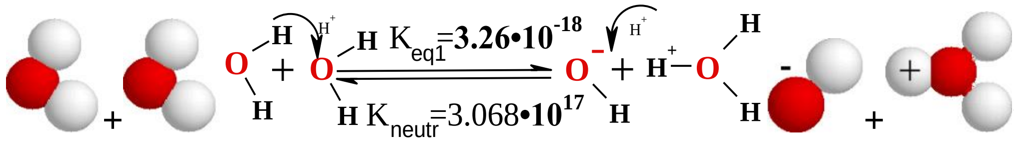


***Fig.4.2. pH** values of some well-known liquids*

Biological medium	**pH**	**Biological medium name**	**pH**
plasma of blood	**7.4**	**Urine**	**4.80÷6.85**
extract of blood	**7.35÷7.45**	**Juice from surrounding of Skin tissues**	**6.20÷7.50**
		Skin surface antibacterial defense pH	**5.5**
Saliva	**6.35÷6.85**	**Gland juice behind of stomach**	**7.80÷8.00**
poor gastric liquor	**0.90÷1.50**	**Lemon juice**	**2.3**
pH of stomach	**1.20÷3.00**	**Tomatoes juice**	**4.3**

Water protolysis and neutralization inverse attractors of reaction:

1^{st} reaction equilibrium $H_2O + H_2O + \Delta H_{ionisation} + \Delta G_{ionisation} <=> OH^{-} + H_3O^{+}$



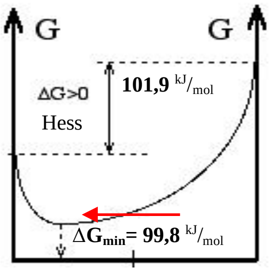
$$;K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3.26\bullet10^{-18}$$

Hess Free energy change for 1^{st} reaction - protolysis is positive, unfavored, endoergic and non spontaneous: $\Delta G_{protolysisHess}=\Delta H_{protolysisHess}-T\Delta S_{protolysisHess}=101{,}9\ ^{kJ}/_{mol}$.

$\Delta G_{eq1}= -R\bullet T\bullet \ln(\mathbf{K_{eq1}})= -8.3144*298.15*\ln(3.26*10^{-18})=\mathbf{99.8}\ ^{kJ}/_{mol}$,

Hess Free energy change $\Delta\mathbf{G}_{Hess}$ is greater, but minimizes reaching equilibrium mixture $99{,}8\ ^{kJ}/_{mol} = |\Delta G_{eq1}| < |\Delta G_{Hess1}| = 101{,}9\ ^{kJ}/_{mol}$;

Water protolysis increases free energy content for water 2 H_2O from zero 0 to 99.8 $^{kJ}/_{mol}$ for protolysis products, what have lost in neutralization.

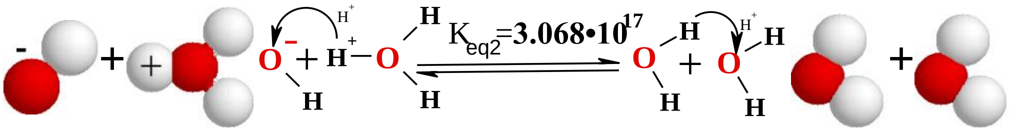


A+B 50% C+D

reactants H_2O+H_2O _

products $H_3O^++OH^-$

2^{nd} reaction equilibrium $OH^- + H_3O^+ <=> H_2O + H_2O + \Delta H_{neutralisation} + \Delta G_{neutralisation}$



$$;K_{eq2}=\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}=\mathbf{3.068\bullet10^{17}}$$

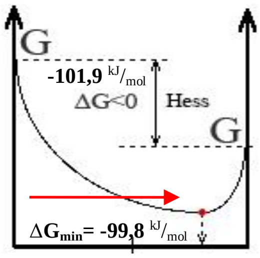
Hess Free energy change for 2^{nd} reaction is negative, favored, exoergic, and spontaneous:

$\Delta G_{neutralizationHess}=\Delta H_{neutralizationHess}-T\Delta S_{neutralizationHess}= \mathbf{-101.9}\ ^{kJ}/_{mol}$;

$\Delta G_{eq2} = \mathbf{-} R\bullet T\bullet \ln(\mathbf{K_{eq2}}) = -8.3144*298.15*\ln(3.068*10^{17})= \mathbf{-99.8}\ ^{kJ}/_{mol}$,

Hess Free energy change $\Delta\mathbf{G}_{Hess}$, is greater, but minimizes reaching mixture of compounds $K_{eq1}=3.26\bullet10^{-18}$; $K_{eq2}=3.068\bullet10^{17}$ at equilibrium.

$$99.8\ ^{kJ}/_{mol} = |\Delta G_{eq1}| < |\Delta G_{Hess1}| = 101.9\ ^{kJ}/_{mol}.$$



A+B 50% C+D

reactants $H_3O^++OH^-$

products $\mathbf{H_2O+H_2O}$

All reactions trend to Prigogine attractor minimum of free energy change $\Delta\mathbf{G}_{min}=\Delta\mathbf{G}_{eq}$ at equilibrium mixture with reverse reactions inverse

constants $3.26\bullet10^{-18}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=K_{eq1}=\frac{1}{K_{eq2}}=\frac{1}{\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}}=\frac{1}{3{,}068*10^{17}}$ for.

In 1977 declared Ilya Prigogine attractors claim perfect order trends of Universe for each process to energy change minimum in mixture of reacting compounds. 15th page

Multiply with water constant concentration square $K_{eq1}*[\mathbf{H_2O}]^2 = 3.26\bullet10^{-18}*55{,}33^2=10^{-14}=K_w$,

one calculates water ions factorial constant $K_w = [\mathbf{H_3O}^+][\mathbf{OH}^-] = 10^{-14}$,

Solubility products as strong and weak electrolytes **THERMODYNAMICS**

6th page :

Solubility $^{36\,g}/_{100g}$ H_2O, demsity 1.203 $^{g}/_{mL}$, C_{NaCl}= 5.4434 $^{mol}/_{L}$; w%=26.47%;

The ionic crystalline solubility and dissociation of electrolyte **solution** in water (4.1)

crystalline $\mathbf{Na^+Cl^-}$ $\mathbf{\Delta H^o}$ = -411.12 $^{kJ}/_{mol}$; $\mathbf{\Delta S^o}$=72 $^{J}/_{(mol\ K)}$

$\mathbf{H_2O}$	$\mathbf{\Delta H^o}$ = -286 $^{kJ}/_{mol}$;	$\mathbf{\Delta S^o}$=69.956 $^{J}/_{(mol\ K)}$	$\mathbf{\Delta G}$ = -286 $^{kJ}/_{mol}$
$\mathbf{Na^+}_{aqua}$	$\mathbf{\Delta H^o}$ = -240.1 $^{kJ}/_{mol}$;	$\mathbf{\Delta S^o}$=59 $^{J}/_{(mol\ K)}$	$[\mathbf{Na(H_2O)_6}]^+$ evident as aqua
$\mathbf{Cl^-}_{aqua}$	$\mathbf{\Delta H^o}$ = -167.2 $^{kJ}/_{mol}$;	$\mathbf{\Delta S^o}$=56.5 $^{J}/_{(mol\ K)}$	$[\mathbf{Cl(H_2O)_6}]^-$ evident as aqua .

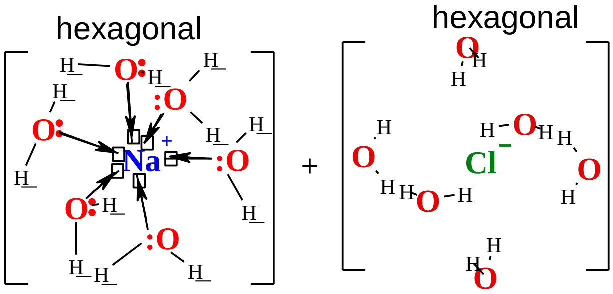
1) the **separation** crystalline sodium chloride $\mathbf{Na^+Cl^-}$ into positive cations $\mathbf{Na^+}$ and into negative $\mathbf{Cl^-}$ anions,

2) When tetramers $\mathbf{(H_2O)_4}$ dismissed the **hydration** with six water molecules coordinated ions $[\mathbf{Na(H_2O)_6}]^+$, $[\mathbf{Cl(H_2O)_6}]^-$.

Crystalline sodium chloride disolutes in water:

$\mathbf{Na^+Cl^-}$+3$\mathbf{(H_2O)_4}$=>[6$\mathbf{H_2O}$:=>□$\mathbf{Na^+}$]$_{aqua}$+[$\mathbf{Cl^-}$<=6$\mathbf{H_2O}$]$_{aqua}$

Overall dissociation process free energy change $\Delta\mathbf{G}$ is:



$\mathbf{\Delta G_{Hess}=\Delta H_{Hess}–T\Delta S_{Hess}}$; **exoergic** $\mathbf{\Delta G_{Hess}}$ = 3.82 - 298.15•43.5/1000 = **-9.15** $^{kJ}/_{mol}$ negative and dissipative dissociation of ionic crystalline is a spontaneous process as water soluble.

Heat accumulates in productes **endothermic** $\mathbf{\Delta H_{HessSum}}$= -240.1-167.2+411.12= +3.82 $^{kJ}/_{mol}$ with cooling effect.

$\mathbf{\Delta S_{dispers}}$=-$\Delta H_{Hess}/T$=-1000•3.82/298.15= -12.812 $^{J}/_{(mol\ K)}$; $\mathbf{\Delta S_{hydratation}}$ = +59+56.5-(72) = +43.5 $^{J}/_{(mol\ K)}$.

Total entropy change in dissipative dissociation of ionic crystalline sodium chloride $\mathbf{Na^+Cl^-}$ into ions $\mathbf{Na^+}$ + $\mathbf{Cl^-}$:

$$\mathbf{\Delta S_{total}=\Delta S_{dispers}} + \mathbf{\Delta S_{hydratation}} = -12.812 + 43.5 = +30.688\ ^{J}/_{(mol\ K)}$$

The overall $\Delta\mathbf{H}$ change in sum is **endothermic**: $\mathbf{\Delta H_{HessSum}=\Delta H=\Delta H^{separation}+\Delta H^{hydration}}$=3.82 $^{kJ}/_{mol}$, where $\mathbf{\Delta H^{separation}>0}$ is positive heat, that supplied for separation of positive and negative ions from each other. Added heat energy $\mathbf{\Delta H^{separation}}$ > **0** is positive value, but $\mathbf{\Delta H^{hydration}}$ the **hydration** process evolved heat **exothermic** $\mathbf{\Delta H^{hydration}<0}$ has negative value.

Salt reaction with **water** is **endothermic** $\mathbf{\Delta H}$=3.82 $^{kJ}/_{mol}$ as salt mixed with melting ice decrees temperature up to -12° C. Freezing suggests positive summary value +3.82 $^{kJ}/_{mol}$ =$\mathbf{\Delta H=\Delta H^{separation}+\Delta H^{hydration}}$

Hess value $\mathbf{\Delta G_{Hess}=\Delta H–T\Delta S_{Hess}}$ is negative because enthalpy change is small $|\mathbf{\Delta H}|$ < $|\mathbf{T\Delta S_{Hess}}|$,

$$\mathbf{K_{sp}}=[\mathbf{Na^+}_{aq}]*[\mathbf{Cl^{-}}_{aq}]/[\mathbf{NaCl}]= =4{,}0952*4{,}0952/1{,}3482=12{,}44$$

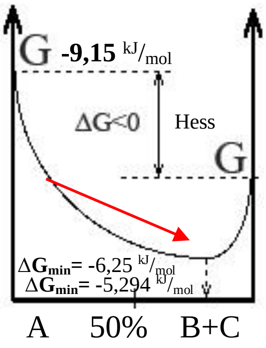
C_{osm}=[$\mathbf{Na^+}$]+[$\mathbf{Cl^-}$]+[$\mathbf{NaCl}$]=i*C_M=(1+ $\boldsymbol{\alpha}$(m-1))*C_M=(1+$\boldsymbol{\alpha}$(2-1))*0,15385=0,305 M. Dissociation degree alpha is fraction $\boldsymbol{\alpha}$ =(0,305/0,15385-1)=0,98245 ar [$\mathbf{NaCl}$]= C_M -C_M*$\boldsymbol{\alpha}$=0,15385-0,15385*0,98245=0,0027 M.

Physiology 0,9% solubility product $\mathbf{K_{0,9\%}}$=[$\mathbf{Na^+}_{aq}$]*[$\mathbf{Cl^-}_{aq}$]/[$\mathbf{NaCl}_{aq}$]=0,151*0,151/0,0027=8,462=$10^{0,927}$;

is favored $\mathbf{\Delta G_{0,9\%}}$= **-R•T•ln**($\mathbf{K_{0,9\%}}$)=-8,3144•298,15•**ln**(8,4616)=-5,294 $^{kJ}/_{mol}$, Solubility product has less favored $\mathbf{\Delta G_{sp}}$=**-R•T•ln**($\mathbf{K_{sp}}$)=-8,3144•298,15•**ln**(12,44)=-6,25 $^{kJ}/_{mol}$.

Endothermic, exoergic crystalin $\mathbf{Na^+Cl^-}_s$ solubility Hess free energy change is negative ΔG_{Hess}=-9,15 $^{kJ}/_{mol}$, but minimizes $\mathbf{\Delta G_{min}}$ =$\Delta G_{0,9\%}$= -8, 4 $^{kJ}/_{mol}$ in mixture reaching equilibrium $\mathbf{K_{0,9\%}}$=[$\mathbf{Na^+}_{aq}$]*[$\mathbf{Cl^{-}}_{aq}$]/[$\mathbf{NaCl}$]=0,1512*0,1512/0,0027=8,462 with products [$\mathbf{NaCl}_{aq}$]= 0,0027 M [$\mathbf{Na^+}_{aqua}$]=[$\mathbf{Cl^-}_{aqua}$]= 0,151 M.

Dissociation degree α=4,0952/5,4434=75,2 % **Crystalic** $\mathbf{Na^+Cl^-}$ reactant compound $\mathbf{K_{sp}}$=[$\mathbf{Na^+}_{aq}$]*[$\mathbf{Cl^{-}}_{aq}$]/[$\mathbf{NaCl}_{aq}$]= 4,0952*4,0952/1,3482=12,44. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium mixture. Free energy change minimum reaching establishes equilibrium.



$\mathbf{Na^+Cl^-}_{aq}$ reactants
products Na^+_{aq}+Cl^-_{aq}

10th page

Strong electrolytes are water soluble salts, water soluble bases and strong acids with $\mathbf{\Delta G<0}$ and $\mathbf{K_{eq}}$ >>**1** ;
Weak electrolytes with positive $\mathbf{\Delta G>0}$ and 0 < $\mathbf{K_{eq}}$ < **1** **endoergic** are water insoluble salts and bases.

Sodium acetate $\mathbf{CH_3COONa}_s \rightleftarrows \mathbf{Na}^+_{aqua}+\mathbf{CH_3COO}^-_{aq}$ solubility product Thermodynamics

$\mathbf{CH_3COONa}_s+8\mathbf{H_2O}$=>[$6\mathbf{H_2O{:}}$=>$\mathbf{Na}^+]_{aq}$ +[$2\mathbf{H_2O}$=>$^-\mathbf{OOCCH}_{3aq}$]

Solubility 50,4 $^g/_{100g}$ H_2O, density 1,26 $^g/_{mL}$, $C_{CH3COONa}$= 5,1493 $^{mol}/_L$; w%= 36,1 %

Litre solution mas with density 1,26 $^g/_{mL}$ is $m_{solution}$ = 1260 $^g/_L$.

What times 150,4 g included 1260 grams solution 1260/150,4= 8,7766...........times .

Sodium acetate mas in litre $m_{CH3COONa}$ =8,7766*50,4 g/100g =442,34..........$^g/_L$..

Molar mas calculates as sum of atomic mases: $M_{CH3COONa}=M_{Na}+M_{CH3COO}$=23+24+32+3= 82 $^g/_{mol}$.

Salt number of mols in one litre is mas of salt over it's molar mas:

$n_{CH3COONa}= m_{CH3COONa} / M_{CH3COONa}$= 442,34 / 82= 5,1493 $^{mol}/_L$; $C_{CH3COONa}$ = 5,1493 $^{mol}/_L$;

Water $m_{H2O}=m_s-m_{CH3COONa}$ =1260-442,34= 817,76 g; $n_{H2O}= m_{H2O} / M_{H2O}$ 817,76/18=45,431 moli..

Mas fraction in perocents : $m_{CH3COONa}/m_{šķ}$=442,34 /1260*100% =w%= 36,1;

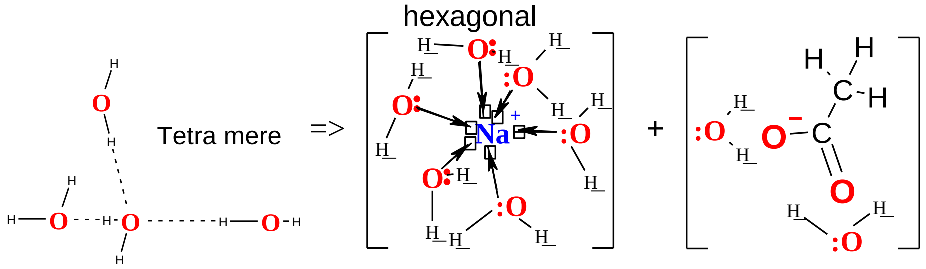
Complete dissociation in ideal solution coordinate 6 $\mathbf{H_2O}$, 2 $\mathbf{H_2O}$ sodium ions and acetate ions crystalline $\mathbf{CH_3COONa}_s \rightleftarrows \mathbf{Na}^+ + \mathbf{CH_3COO}^-$ solie, poore compound mol fraction is one $[\mathbf{CH_3COONa}]_{solid}$ = 1 and solubility producēt constant: $\mathbf{K_{sp}}= \mathbf{K_{eq}}$ =$[\mathbf{Na}^+]$*$[\mathbf{CH_3COO}^-]$=5,1493*5,1493= 26,515 is ions factorial reaching Prigogine attractor at equilibrium free emergy change minimum negative::

Thermodynamic favored solubilty product constant: for favored equilibrium:

$$\mathbf{\Delta G_{min}=\Delta G_{eq}=-R\bullet T\bullet ln(K_{eq})} =-8,3144\bullet 298,15\bullet \mathbf{ln}(26,515)= -8,125\ ^{kJ}/_{mol},$$

Saturated solution water coordination resocres 8 are indispensible: nc= n_{H2O} /8=45,431/8= 5,6789..........moli.

$\mathbf{CH_3COONa}_{aqua} + 2(\mathbf{H_2O})_4$



+ $\mathbf{Q}$ + ΔG;

CRC 2010

Substance	$\Delta H°_{Hess}$, $^{kJ}/_{mol}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$	$\Delta G°_{Hess}$, $^{kJ}/_{mol}$
$\mathbf{Na}^+_{aqua}$	-240,1	59	-
$\mathbf{CH_3COO}^-_{aq}$	-486	85,3	-247.83
$\mathbf{CH_3COO}^-_{aq}$	**-486,836**	**-822,3**	**-241,663**
$\mathbf{CH_3COONa}_s$	-708,8	123,0-	-607,7-

reactant => products

$\mathbf{CH_3COONa}_s$ => $\mathbf{Na}^+_{aqua}+\mathbf{CH_3COO}^-_{aqua}$ +$\mathbf{Q}$ +ΔG;

1. $\Delta H_{Hess}= \Sigma\Delta H°_{products}- \Sigma\Delta H°_{Reactants}$;

2. $\Delta S_{Hess}= \Sigma\Delta S°_{products}- \Sigma\Delta S°_{Reactants}$;3.$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

2. $\Delta S_{dispersed}=-\Delta H_{Hess}/T$=17,3/298,15=58,02448...........$^J/_{mol/K}$;

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}$=58,02448+21,3=79,32448...........$^J/_{mol/K}$;

1. $\mathbf{\Delta H_{Hess}=\Delta H°_{H3CCOO-}+\Delta H°_{Na}-\Delta H°_{H3CCOO\,Na}}$=-486-240,1-(-708,8)= -17,3 $^{kJ}/_{mol}$ **eksotermiska**..................

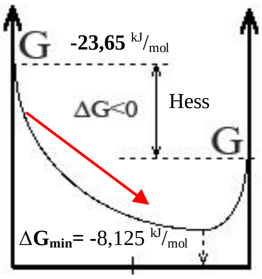
2. $\mathbf{\Delta S_{Hess}=\Delta S°_{H3CCOO-}+\Delta S°_{Na+aqua}-\Delta S°_{H3CCOO\,Na}}$=59+85,3-123= 144,3-123=21,3.......$^J/_{mol/K}$ **eksoerģiska**.............

$\mathbf{\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}}$=-17,3-298.15*0,0213=-23,65........$^{kJ}/_{mol}$;T•ΔS_{total}=79,32448•298,15=**23,65**............$^{kJ}/_{mol}$;

Exothermic and exoergic $\mathbf{CH_3COONa}_s$ solubility product Hess free energy change $\mathbf{\Delta G_{Hess}}$ negative -23,65 $^{kJ}/_{mol}$, but minimizes up to $\mathbf{\Delta G_{min}} = \mathbf{\Delta G_{eq}}$ =-8,125 $^{kJ}/_{mol}$ in mixture reaching solubility product $\mathbf{K_{sp}}= \mathbf{K_{eq}}$= $[\mathbf{Na}^+]$*$[\mathbf{CH_3COO}^-_{aqua}]$ =5,1493*5,1493= 26,515 .

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.



reactant crystalline $\mathbf{CH_3COONa}_s$–A 50% B+C

and products– $\mathbf{Na}^+_{aq}+\mathbf{CH_3COO}^-_{aq}$

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37% **HCl** acid density 1,18 g/mL **HCl** ⇄ $\mathbf{H^+ + Cl^-}_{aqua}$ protolysis- dissociation thermodynamics

$\Delta H_{hydratation\,\mathbf{HCl}}=\Delta H^\circ_{\mathbf{HCl}aqua}-\Delta H^\circ_{\mathbf{HCl}gas}=-167{,}2-(-92{,}31)=-74{,}89$.......... $^{kJ}/_{mol}$ **exothermic**...................

CRC 2010 Reaction is **exothermic** , **athermic**, **endothermic**,**exoergic**, **endoergic**! ?$\mathbf{HCl}_{gas}$**=>**$\mathbf{HCl}_{aqua}$+ΔG+**Q**;

Substance	ΔH°_H, $^{kJ}/_{mol}$	ΔS°_H, $^{J}/_{mol/K}$	ΔG°_H, $^{kJ}/_{mol}$
Na+Cl-	-411,12	72,00	-
$\mathbf{Na+}_{aqua}$	-240,10	59,00	-
$\mathbf{Cl\text{-}}_{aqua}$	-167,2	56,50	**-183,955**
$\mathbf{H_2O}_{aq}$	-285,85	69,956	-237,191
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{HCl}_{gas}$	-92,31	186,902	-95,3
$\mathbf{HCl}_{aqua}$	-167,2	56,5	-131,2

$\Delta G_H=\Delta G^\circ_{\mathbf{HCl}aqua}-\Delta G^\circ_{\mathbf{HCl}gas}=-131{,}2-(-95{,}3)=-35{,}9$............ $^{kJ}/_{mol}$

1. $\Delta H_{Hess}=\Sigma\Delta H^\circ_{products}-\Sigma\Delta H^\circ_{Reactants}$; **exoergic**..................

$\Delta H_{hydratation\,\mathbf{HCl}}=\Delta H^\circ_{\mathbf{HCl}aqua}-\Delta H^\circ_{\mathbf{HCl}gas}=-167{,}2-(-92{,}31)=-74{,}89$........ $^{kJ}/_{mol}$

$\Delta G_{Cl-}=\Delta H_H-T*\Delta S_H=-167{,}08-298{,}15*0{,}0566=\mathbf{-183{,}955}$ $^{kJ}/_{mol}$;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=251{,}182-130{,}4=120{,}78$....... $^{J}/_{mol/K}$;

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{HCl}aqua}-\Delta S^\circ_{\mathbf{HCl}gas}=56{,}5-186{,}902=-130{,}402$........ $^{J}/_{mol/K}$;

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=74{,}89/298{,}15=251{,}182$........ $^{J}/_{mol/K}$;

3. $\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}=-74{,}89-298{,}15*-0{,}130=-36{,}01$....... $^{kJ}/_{mol}$

Bound energy $T\bullet\Delta S_{total}=120{,}78$ $^{J}/K/_{mol}\bullet298{,}15$ K=**36,01**....... $^{kJ}/_{mol}$;exoergic....................

37%, 1,180 g/mL, 436,6 g/36,45=11,978 $^{mol}/_L$, 1180-436,6=743,4;743,4/18=41,3 $^{mol}/_L$, 41,3-0,25236=41,048 $^{mol}/_L$

$\mathbf{HCl+H_2O=>H_3O^+}_{(aq)}\mathbf{+Cl^-}_{aqua}$ +**Q** +ΔG; $\mathbf{HCl=>H^++Cl^-}_{aqua}$; $[\mathbf{H_3O^+}]^2+[\mathbf{H_2O}]*\mathbf{K_{dis}}*[\mathbf{H_3O^+}]-\mathbf{K_{dis}}*[\mathbf{H_2O}]*11{,}978=0$

$\Delta H_{Hess}=\Delta H^\circ_{\mathbf{H3O}}+\Delta H^\circ_{\mathbf{Cl-}}-\Delta H^\circ_{\mathbf{HCl}aq}-\Delta H^\circ_{\mathbf{H2O}}=-285{,}81-167{,}08-(-167{,}2-285{,}85)=0{,}16$........ $^{kJ}/_{mol}$; **athermic**..............

2. $\Delta S_{dispersed}=-\Delta H_{Hess}/T=-0{,}16/298{,}15=-0{,}537$........... $^{J}/_{mol/K}$

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{H3O}}+\Delta S^\circ_{\mathbf{Cl-}}-\Delta S^\circ_{\mathbf{HCl}}-\Delta S^\circ_{\mathbf{H2O}}=-3{,}854+56{,}60-(69{,}96+56{,}5)=52{,}64-126{,}46=-73{,}714$......... $^{J}/_{mol/K}$

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=-0{,}537-73{,}714=-74{,}251$........ $^{J}/_{mol/K}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=0{,}16-298.15*-0{,}073714=22{,}1378$.............. $^{kJ}/_{mol}$ **endoergic**..........................

$T\bullet\Delta S_{total}=-74{,}251$ $^{J}/K/_{mol}\bullet298{,}15$ K=**-22,14**...... $^{kJ}/_{mol}$;

$\underline{m_{\mathbf{H2O}}=1180-436{,}6=743{,}4\text{ g;}}$ $n_{\mathbf{H2O}}=743{,}4/18=41{,}3$ $^{mol}/_L$, First solution:

$[\mathbf{H_2O}]=41{,}3-[\mathbf{H_3O^+}_{aq}]=41{,}3-0{,}25235=41{,}047664$ $^{mol}/_L$’ $C_{\mathbf{HCl}}=[\mathbf{HCl}_{aqua}]+[\mathbf{Cl^-}]=11{,}978$ M ;

$[\mathbf{HCl}_{aqua}]=(11{,}978-[\mathbf{Cl^-}])=(11{,}978-0{,}25235)=11{,}725664$ $^{mol}/_L$;

$[\mathbf{H_2O}]=41{,}3-0{,}2578=41{,}0422$ $^{mol}/_L$ $[\mathbf{HCl}_{aqua}]$ $[\mathbf{H_2O}]*\mathbf{K_{dis}}=[\mathbf{H_3O^+}_{aq}]*[\mathbf{Cl^-}_{aqua}]$;

As equal $[\mathbf{Cl^-}_{aqua}]=[\mathbf{H_3O^+}_{aq}]$ and replased $[\mathbf{Cl^-}_{aqua}]$ with $[\mathbf{H_3O^+}_{aq}]$ square equation is solved as: $ax^2+bx+c=0$.

$(11{,}978-[\mathbf{Cl^-}])\,[\mathbf{H_2O}]*\mathbf{K_{dis}}=[\mathbf{H_3O^+}]*[\mathbf{Cl^-}_{aqua}]$; $(11{,}978-[\mathbf{H_3O^+}])\,[\mathbf{H_2O}]*\mathbf{K_{dis}}=[\mathbf{H_3O^+}]*[\mathbf{H_3O^+}]$;

$[\mathbf{H_3O^+}]^2+[\mathbf{H_2O}]*\mathbf{K_{dis}}*[\mathbf{H_3O^+}]-\mathbf{K_{dis}}*[\mathbf{H_2O}]*11{,}978=0$

Square equation $ax^2+bx+c=0$ solves real root of two mathematic $\mathbf{x}=\left(\frac{-b+\sqrt{b^2-4ac}}{2a}\right)$;

$$\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}_{aq}]=\frac{-K_{dis}\cdot[H_2O]+\sqrt{(K_{dis}*[H_2O])^2-4*-K_{dis}*[H_2O]*11{,}978}}{2}=0{,}25235\text{............M}$$

$$[\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}]=\left(\frac{-1{,}323*10^{-4}*41{,}04765+\sqrt{(1{,}323*10^{-4}*41{,}04765)^2-4*-1{,}323*10^{-4}*41{,}04765*11{,}978}}{2}\right)=0{,}25235\text{.........M}$$

Dissociation degree $\boldsymbol{\alpha}$**=0,021**=$\mathbf{C_{dis}/C_M}$=0,25236/11,978; $\mathbf{C_M=C_{dis}+C_{nedis}}$=0,25236 + 11,725664=11,978 $^{mol}/_L$;

Equilibrium constant $\frac{[H_3O^+]aqua\cdot[Cl^-]\,aqua}{[HCl]aqua\cdot[H_2O]}$ =$\mathbf{K_{eq}}$=(0,2523*0,2523)/(41,0476*11,725664)=$1{,}323*10^{-4}$;

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}=-8{,}3144\bullet298{,}15\bullet\mathbf{ln}(0{,}0001323)=22{,}138$ $^{kJ}/_{mol}$,

Unfavored protolysis Hess law positive 22,14 $^{kJ}/_{mol}$, but minimized reaching equilibrium 22,138 $^{kJ}/_{mol}$.

Hydro chloric concentration is $C_{\mathbf{HCl}}=[\mathbf{HCl}_{aqua}]+[\mathbf{Cl^-}]=0{,}1$ M ; $[\mathbf{H_2O}]=53{,}23-[\mathbf{H_3O^+}_{aq}]=53{,}33-0{,}1=53{,}23$ $^{mol}/_L$

$$[\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}]=\left(\frac{-7{,}681*10^{-4}*53{,}2+\sqrt{(7{,}681*10^{-4}*53{,}2)^2-4*-7{,}681*10^{-4}*53{,}2*0{,}1}}{2}\right)=0{,}04729\text{..........M}$$

Equilibrium constant $\frac{[H_3O^+]aqua\cdot[Cl^-]\,aqua}{[HCl]aqua\cdot[H_2O]}$ =$\mathbf{K_{eq}}$=(0,04729*0,04729)/(53,2*0,05271)=$7{,}681*10^{-4}$;

$[\mathbf{H_3O^+}]=0{,}04729$..........M $=10^{-pH}=10^{-1{,}325}$; pH= $-\log[\mathbf{H_3O^+}_{aq}]=-\log\mathbf{0{,}04729}=1{,}325$..............;

Dissociation degree: $\boldsymbol{\alpha}$**=** $\mathbf{C_{dis}/C_M}$ =0,04729/0,1=0,473 , **α%=** 47,3......... %

$\Delta G_{Hess}=22{,}14$........... $^{kJ}/_{mol}$ **endoergic**.............Prigogine minimum $\Delta\mathbf{G}_{\mathbf{eq}0{,}1HCl}=17{,}8$.......... $^{kJ}/_{mol}$,

11th page:

Ammonium chloride $NH_4Cl_{(s)}$ => $NH_4^+{}_{(aq)}$+ $Cl^-{}_{aqua}$ electrolyte thermodynamic solubility in water

Data from tables: solubility 39,5 $^g/_{100g}$ H_2O, density 1,3536 $^g/_{mL}$, weak acid NH_4^+ pK_a=9,25 protolysis

$NH_{3\ (aq)}$+H_2O=>NH_4^++OH^- strong protolytic base pK_b=4,74 > 9,25=pK_a weak NH_4^++H_2O=>$NH_{3\ (aq)}$+H_3O^+ ;

Liter solution mass with density 1,3536 $^g/_{mL}$ is $m_{solution}$ = 1353,6 ....$^g/_L$.

What times 139,5 g include 1353,6 grams solution 1353,6/139,5= 9,7032............times

Amonium chloride mas in litre m_{NH4Cl} = 9,7032 *39,5 g/100g = 383,2764..........$^g/_L$..

Molar mas is sum of atomic mases: M_{NH4Cl}=M_{NH4}+M_{Cl}=16+24+35,5= 75,5...........$^g/_{mol}$.

Salt number of mols in litre is salt mas over it's molar mas:

n_{NH4Cl}= m_{NH4Cl} / M_{NH4Cl}= 383,2764 / 75,5= 5,07651 $^{mol}/_L$; C_{NH4Cl}= 5,07651.........$^{mol}/_L$;

Water m_{H2O}=$m_{šķ}$-m_{NH4Cl} = 1353,6-383,2764=970,32 g n_{H2O}= m_{H2O} / M_{H2O} =970,32/18=53,907.........moli.

Mas fratio in percents is mas of salt over solution mas :

m_{NH4Cl}/$m_{šķ}$=383,2764/1353,6*100% =w%=28,32...........%;

Thermodynamic favored complete dissolution reaction by Hes law and solubility constant .

Substance	$\Delta H°_{Hess}$,$^{kJ}/_{mol}$	$\Delta S°_{Hess}$,$^J/_{mol/K}$	$\Delta G°_{Hess}$,$^{kJ}/_{mo}$
$Cl^-{}_{aqua}$	-167,2	56,50	**-183,955**
$NH_4^+{}_{(aq)}$	-132,5	113,4	-
$NH_4Cl_{(s)}$	-314,4	94,6-	-202,97

reactants $NH_4Cl_{(s)}$ +**Q** => $NH_4^+{}_{(aq)}$+ $Cl^-{}_{aqua}$ +ΔG products;

ΔG_{Cl-}=ΔH_H–T*ΔS_H=-167,08-298,15*0,0566=**-183,955** $^{kJ}/_{mol}$;

2. ΔS_{Hess}= $\Sigma\Delta S°_{products}$- $\Sigma\Delta S°_{Reactants}$**;**

CRC 2010 3. ΔG_{Hess}= ΔH_{Hess}-T•ΔS_{Hess}

1. ΔH_{Hess}=$\Delta H°_{NH4}$+$\Delta H°_{Cl}$-$\Delta H°_{NH4Cls}$= -132,5-167,2-(-314,4)=-299,7+314,4=14,7.......$^{kJ}/_{mol}$ **endothermic**.........
2. $\Delta S_{dispersed}$=-ΔH_{Hess}/T=-14,7/298,15=-49,3........$^J/_{mol/K}$;
2. ΔS_{Hess}=$\Delta S°_{NH4}$+$\Delta S°_{Cl}$-$\Delta S°_{NH4Cl}$= 113,4 +56,50-(94,6)= 169,9-94,6=75,3..........$^J/_{mol/K}$
3. ΔS_{total}= ΔS_{Hess}+ $\Delta S_{dispersed}$=-49,3+75,3= 26........$^J/_{mol/K}$;

ΔG_{Hess}=ΔH_{Hess}-T*ΔS_{Hess}=14,7-298,15*0,0753=-7,75..........$^{kJ}/_{mol}$; **exoergic**.............................

T•ΔS_{total}=26 $^J/K/_{mol}$•298,15 K=**7,75**........$^{kJ}/_{mol}$;

$$\frac{[NH_4^+]_{aqua}\cdot[Cl^-]_{aqua}}{[NH_4Cl]_{aqua}} = \mathbf{K_{spHess}} = \mathbf{exp(-\Delta G_{Hess}/R/T)} = exp(7,75/8,3144/298,15)=22,8.......$$

Thermodynamic favored Hess solubility product in water .

Complete dissociation solubility product constant

K_{dis}=[$NH_4^+{}_{aq}$]*[$Cl^-{}_{aqua}$]= 5,07651*5,07651=25,771..........

Amonium chloride K_{spHess}=22,8 non dissociated concentration is calculated in expression :

[NH_4Cl_{aqua}]= [$NH_4^+{}_{aq}$]*[$Cl^-{}_{aqua}$]/ K_{spHess}=25,771/22,8= 1,13.......$^{mol}/_L$,

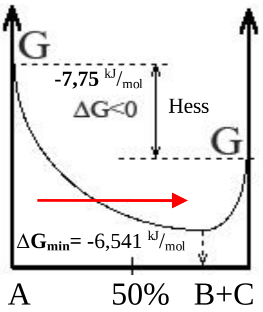
including equal dissociated ions concentration in subtraction solubility concentration minus non dissociated salt concentration: [$NH_4^+{}_{(aq)}$]=[$Cl^-{}_{aqua}$]= 5,07651-1,13=3,97651 ....$^{mol}/_L$,

Favored solubility product constant: $\mathbf{K_{eq}}=\dfrac{[NH_4^+]_{aqua}\cdot[Cl^-]_{aqua}}{[NH_4Cl]_{aqua}}$ =3,97651*3,97651/1,13= 13,9935...........

ΔG_{eq}=**-R•T•ln**(K_{eq})=-8,3144•298,15•**ln**(13,9935)= -6, 541 ....$^{kJ}/_{mol}$, Endothermic and exoergic $NH_4Cl_{(s)}$ dissociation Hess free energiy change $\Delta G_{disHess}$=-7,75 ....$^{kJ}/_{mol}$ negative, but minimized reaching ΔG_{min}=ΔG_{eq}= -6, 541.........$^{kJ}/_{mol}$ equilibrium mixture

$$\mathbf{K_{eq}}=\frac{[NH_4^+]_{aqua}\cdot[Cl^-]_{aqua}}{[NH_4Cl]_{aqua}} = 13,9935\mathbf{..........}$$

reactant non dissociated ammonium chloride NH_4Cl_{aqua}_ and products $NH_4^+{}_{aqua}$ + $Cl^-{}_{aqua}$



Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium. 13th page

In human organism weak electrolytes are carbonic acids, amino acids, protonate amines:

If ΔG is positive, **e** is taken into a negative power $\mathbf{e}^{-negative}$ in calculation of $\mathbf{K_{dis}}$, therefore $\mathbf{K_{dis}}$ much smaller then **1** ($\mathbf{0 < K_{dis} << 1}$) and never reach the zero **0**. In this case the acids are weak in human body.

Carboxylic acid - COOH dissociation-protolysis thermodynamics

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Viela	$\Delta H°_H$, kJ/mol	$\Delta S°_H$, J/mol/K	$\Delta G°_{Hess}$, kJ/mo
$\mathbf{H_3O^+}$	-285.81	-3.854	-213,275
$\mathbf{H_3CCOO^-}$	-486	85.3	85.3
$\mathbf{CH_3COO^-_{aq}}$	**-486,836**	**-822,3**	**-241,663**
$\mathbf{H_2O}$	-285.85	69.9565	69.9565
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
H3C-COOH	-484,09	159,83	-531,743

Reactants => products

$$\mathbf{CH_3COOH+H_2O+\Delta G \Leftrightarrow H_3O^+ + CH_3COO^{-} + Q}$$

1. $\Delta H_{Hess} = \Delta H°_{products} - \Delta H°_{reactants}$
2. $\Delta S_{Hess} = \Delta S°_{products} - \Delta S°_{reactants}$
3. $\Delta G_{Hess} = \Delta H_{Hess} - T \bullet \Delta S_{Hess}$

Biochemical Thermodynamic 2006 Alberty

Masachusetts Technology Institute

1. $\Delta H_r = \Delta H°_{H3CCOO-} + \Delta H°_{H3O} - \Delta H°_{H2O} - \Delta H°_{H3CCOOH}$ =..kJ/mol;
.......................=-486-285,81-(-285,85-484,09) =-771,81+769,94= -1,87 kJ/mol **exothermic**.................................

2. $\Delta S_{disperse} = -\Delta H_r / T$ =1,87/298,15= 6,272011 .... J/(mol K)....

2. $\Delta S_r = \Delta S°_{H3CCOO-} + \Delta S°_{H3O} - \Delta S°_{H2O} - \Delta S°_{H3CCOOH}$ =..J/mol/K...
.........=85,3-3,854-(69,9565+159,83)= 81,446-229,7865= -148,3405..J/mol/K;

3. $\Delta S_{total} = \Delta S_r + \Delta S_{disperse}$= -148,3405+6,272011= -142,0685... J/(mol K)....

$\Delta G_r = \Delta H_r - T^*\Delta S_r$ =-1,87+298,15*0,1483405 = 42,3577............................kJ/mol **endoergic**.................

3. $T \bullet \Delta S_{total}$=-142,0685J/K/mol•298,15 K= **-42,3577**...kJ/mol;

bound TΔSn← accumulated energy $\Delta G_{reverseHess}$ ←Q= 1,87.........kJ/mol..non **spontaneous** ΔG_r= 42,4 kJ/mol...........

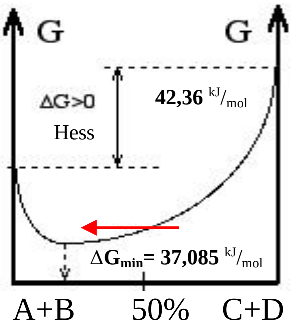
Equilibrium reached by free energy minimum at compounds mixture ratio in expression:

Thermodynamic unfavored equilibrium constant $\mathbf{K_{eq}} = \dfrac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nedis}}$ =1,76*10-5/55,3 =10-6,497

$$\mathbf{\Delta G_{eq} = -R \bullet T \bullet ln(K_{eq})} = -8{,}3144 \bullet 298{,}15 \bullet \mathbf{ln}(10^{-6{,}497}) = 37{,}085 \text{ kJ/mol},$$

Endothermic and endoergic acetic acid protolytic reaction Hess free energy change $\mathbf{\Delta G_{protolyse}}_{Hess}$ =42,36 kJ/mol positive, but minimizes up to $\mathbf{\Delta G_{min} = \Delta G_{eq}}$=37,085 kJ/mol reaching equilibrium mixture :

$$\mathbf{K_{eq}} = \frac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nedis}} = 10^{-6{,}497}\ .$$



reactants mixture_ $\mathbf{CH_3COOH+H_2O}$

products_ $\mathbf{H_3O^+ + CH_3COO^{--}}$

Dissociation constant of acetic acid $\mathbf{K_a = K_{H3CCOOH} = K_{eq}[H_2O]} = \dfrac{[H^+]\cdot[CH_3COO^-]}{[CH_3COOH]_{nedis}}$ =10-6,497*55,3=10-4,76; is

thermodynamic constsnt $\mathbf{K_{eq}}$ multiplication with water constant concentration $\mathbf{[H_2O]}$= 55,3 M make $\mathbf{K_a}=10^{-4{,}76}$.

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.

$\mathbf{[H_3O^+]=[CH_3COO^-]}$=C*$\boldsymbol{\alpha}$=0,2*0,00931=$10^{-2{,}73}$ M =1,862*10^{-3} M; $\boldsymbol{\alpha}$=$10^{-2{,}73}$/0,2=0,00931 ; 14th page:

Ammonia water and ammonium ion $\mathbf{NH_4^+}_{(aq)}$ $+\mathbf{H_2O}+\Delta G+\mathbf{Q} => \mathbf{NH_3}_{\,(aq)}+\mathbf{H_3O^+}$ protolysis Thermodynamics

$\mathbf{NH_3}_{\,(aq)}+\mathbf{H_2O}=>\mathbf{NH_4^+}+\mathbf{OH^-}$ strong protolytic base $pK_b=4,74 > 9,25=pK_a$ weak $\mathbf{NH_4^+}+\mathbf{H_2O}=>\mathbf{NH_3}_{\,(aq)}+\mathbf{H_3O^+}$;

1. Hydration; $\mathbf{NH_{3gas}}+\Delta G =>\mathbf{NH_{3aq}} +\mathbf{Q}$;

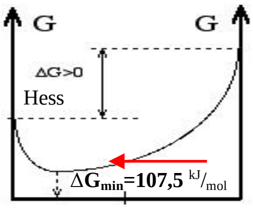
$\Delta H_{hydrationHess}=\Delta H°_{\mathbf{NH3aqua}}\mathbf{-}\Delta H°_{\mathbf{NH3gas}} =\mathbf{-132,5608}-(-45,94)= -86,6\ ^{kJ}/_{mol}$;

$\Delta G_{HydrationHess}=\Delta G°_{\mathbf{NH3aqua}}\mathbf{-}\Delta G°_{\mathbf{NH3gas}}=\mathbf{91,1056}-(-16,4)=107,5\ ^{kJ}/_{mol}$;

$\mathbf{\Delta S_{HydrationHess}=\Delta S°}_{NH3aqua}\mathbf{-\Delta S°}_{NH3gas}\mathbf{=-739,2922}-192,77= -932,0622..........^{J}/_{mol/K}$;

$\mathbf{\Delta G}_{Hess}=\mathbf{\Delta H}_{Hess}\mathbf{-T*\Delta S}_{Hess} =-86,6-298,15*-0,9320622 =191,3.............\ ^{kJ}/_{mol}$;

$K_{eq1}=\exp(\mathbf{-\Delta G_{Hess}}/R/T\mathbf{)}=\exp(-107500/8,3144/298,15)=10^{-18,83}$;



A 50% B

reactant $\mathbf{NH_{3gas}}$

products $\mathbf{NH_{3aq}}$

Ammonia NH_{3aq} protonation reaction with water

2. K_{eq2}**; Ammonia water** $NH_{3\mathbf{aq}}+ H_2O +Q=> NH_4^+{}_{\mathbf{aq}}\mathbf{+}\ OH^- \mathbf{+\Delta G}$

$\mathbf{\Delta H}_{Hess}\mathbf{=\Delta H°}_{\mathbf{NH4+}}\mathbf{+\Delta H°}_{\mathbf{OH}}\mathbf{-\Delta H°}_{\mathbf{NH3}}\mathbf{-\Delta H°}_{\mathbf{H2O}}\mathbf{=-132.5608}-230.015-(-132.5-285.85)=\mathbf{55.8}\ ^{kJ}/_{mol}$ **endothermic**

Viela	$\Delta H°_H$, $^{kJ}/_{mol}$	$\Delta S°_H$, $^{J}/_{mol/K}$	$\Delta G°_H$, $^{kJ}/_{mol}$
$\mathbf{H_3O^+}$	-285.81	-3.854	-213.275
$\mathbf{H_2O}$	-285.85	69.9565	-237.191
$\mathbf{H_2O}$	**-286.65**	**-453.188**	**-151.549**
$\mathbf{NH_4^+}$	-132.5	113.4	-79.3
$\mathbf{NH_{3aq}}$	**-132.5608**	**-739.2922**	**91.1056**
$\mathbf{NH_{3gas}}$	-45.94	192.77	-16.4
$\mathbf{OH^-}$	–230.015	–10.539	-157.2

$1.\Delta H_{Hess}=\Sigma\Delta H°_{products}-\Sigma\Delta H°_{reactants};3.\Delta G_{Hess}= \Delta H_{Hess}-T•\Delta S_{Hess}$

CRC 2010; $2.\ \Delta S_{Hess}= \Sigma\Delta S°_{products}- \Sigma\Delta S°_{reactants}$

$\Delta S_{dispersed}=-\Delta H_H/T=\mathbf{-55.77}/298.15*1000=\mathbf{-187}\ ^{J}/_{(mol\ K)}$;

$\Delta S_{Hess}\mathbf{=\Delta S°}_{\mathbf{NH4+}}\ \mathbf{+\Delta S°}_{\mathbf{OH}}\mathbf{-\Delta S°}_{\mathbf{NH3}}\mathbf{-\Delta S°}_{\mathbf{H2O}}\mathbf{=771.8}\ ^{J}/_{mol/K}$;

$=113,4-10,9-(\mathbf{-739,2922}+69,9565)\mathbf{=771,8}\ ^{J}/_{mol/K}$;

BioTherm2006; $\Delta S_{total}=\Delta S_H+ \Delta S_{dispersed}\mathbf{=-187+771,8=584,8}\ ^{J}/_{(mol\ K)}$;

$\mathbf{\Delta G}_{Hess}\mathbf{=\Delta H}_{Hess}\mathbf{-T*\Delta S}_{Hess}\mathbf{=55,77}-298,15*\mathbf{0,7718=-174,3}\ ^{kJ}/_{mol}$.

$T•\Delta S_{total}\mathbf{=0,5848}*298,15\mathbf{=174,4}\ ^{kJ}/_{mol}$.; bound energy;

$\Delta G_{min}\mathbf{=\Delta G°}_{\mathbf{NH4+}}\mathbf{+\Delta G°}_{\mathbf{OH}}\mathbf{-\Delta G°}_{\mathbf{NH3}}\mathbf{-\Delta G°}_{\mathbf{H2O}}=-79,3-157,2-(\mathbf{91,1056}-237,191)\mathbf{=-90.4146}\ ^{kJ}/_{mol}$ **exoergic**.

$K_{eq2}=\exp(\mathbf{-\Delta G_{min}}/R/T\mathbf{)=}\exp(90414,6/8.3144/298.15)=10^{15.84}$; favored reaction strong base.

Hesss change negative $\Delta G_{Hess}\mathbf{=-329.4}\ ^{kJ}/_{mol}$ minimized at equilibrium mixture $\Delta G_{min}\mathbf{=-90,4}\ ^{kJ}/_{mol}$;

3. $\mathbf{K_{eq3}}$; protolysis $\mathbf{NH_4^+}{}_{aq}\mathbf{+H_2O}+\Delta G+Q\mathbf{=>NH_{3}}{}_{aq}\mathbf{+H_3O^+}$; $\mathbf{NH_4^+}= H^+ + \mathbf{NH_{3}}{}_{aqua}$; $pK_a=9,25$;

$1.\Delta H_H\mathbf{=\Delta H°}_{\mathbf{NH3}}\mathbf{+\Delta H°}_{\mathbf{H3O}}\mathbf{-\Delta H°}_{\mathbf{NH4+}}\mathbf{-\Delta H°}_{\mathbf{H2O}}=-132,5-285,81-(\mathbf{-132,5608-286,65})=0,901.........^{kJ}/_{mol}$ **athermic**......

$2.\Delta S_{dispersed}=-\ \Delta H_H/T=-0,901/298.15= -3,02........^{J}/_{(mol\ K)}$; $\mathbf{\Delta G}_{Hess}\mathbf{=\Delta G°}_{\mathbf{NH3}}\mathbf{+\Delta G°}_{\mathbf{H3O}}\mathbf{-\Delta G°}_{\mathbf{NH4+}}\mathbf{-\Delta G°}_{\mathbf{H2O}}\mathbf{=108,7}\ ^{kJ}/_{mol}$

$2.\ \mathbf{\Delta S}_{Hess}\mathbf{=\Delta S°}_{\mathbf{NH3}}\mathbf{+\Delta S°}_{\mathbf{H3O}}\mathbf{-\Delta S°}_{\mathbf{NH4+}}\mathbf{-\Delta S°}_{\mathbf{H2O}}\mathbf{=-739,2922}-3,854-(113,4\mathbf{-453,188})= -403,4..........^{J}/_{mol/K}$

$\mathbf{\Delta G}_{Hess} = \mathbf{\Delta H}_{Hess} – T*\mathbf{\Delta S}_{Hess} =0,9008-298,15*-0,4033582 =121,2.........^{kJ}/_{mol}$.**endoergic**...............

$\Delta S_{total}= \Delta S_{Hess}+\Delta S_{dispersed}=-3,021-403,358=-406,4.......\ ^{J}/_{(mol\ K)}$ $T•\Delta S_{total}=-406,4*298,15=\mathbf{-121,2}........^{kJ}/_{mol}$;

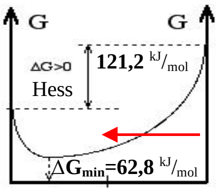
$$\mathbf{K_{eq2}} = \frac{[OH^-]aqua\cdot[NH_4^+]aqua}{[NH_3]aqua\cdot[H_2O]} =10^{15,84} \text{ strong base; } .\mathbf{K_{eq3}}= \frac{[NH_3]aqua\cdot[H_3O^+]}{[NH_4^+]aqua\cdot[H_2O]}=1,013*10^{-11} \text{ weak acid;}$$

$$\text{Thermodynamic constant: } \mathbf{K_{eq3}=[H_2O]*K_{H2O}/K_{NH4OH}=[H_2O]}\ \frac{3.26*10^{-18}}{1,78*10^{-5}}=55,3*1,831*10^{-13}=1,013*10^{-11};$$

$$\text{Acid constant } \mathbf{K_a}= \frac{[H^+]\cdot[NH_3]aqua}{[NH_4^+]aqua} = \mathbf{[H_2O]*K_{eq3}}=55,3*1,014*10^{-11}=5,61176*10^{-10}=10^{-9,25}=10^{pKa} \text{ ; } pK_a=9,25;$$

$\mathbf{\Delta G_{eq3}}=-R•T•\ln(\mathbf{K_{eq3}})=-8,3144•298,15•\ln(1,014*10^{-11})=62,76\ ^{kJ}/_{mol}$, Endothermic and exoergic $\mathbf{NH_4^+}{}_{aq}$ protolysis Hess free energy change $\mathbf{\Delta G_{protolysisHess3}}=121,2\ ^{kJ}/_{mol}$ is positive, but minimized to $\mathbf{\Delta G_{eq3}}=62,76\ ^{kJ}/_{mol}$ reaching equilibrium mixture

$$\mathbf{K_{eq3}}= \frac{[NH_3]aqua\cdot[H_3O^+]}{[NH_4^+]aqua\cdot[H_2O]}=1,013*10^{-11}.$$



A+B 50% C+D

$\mathbf{NH_4^+}{}_{\mathbf{aq}}\mathbf{+H_2O}$

reactants_

$\mathbf{NH_{3aq}+H_3O^+}$

products

Endothermic and exoergic $\mathbf{NH_{3aq}}$ and $\mathbf{H_2O}$ ionization free energy change $\mathbf{\Delta G_{protolysisHess}}$ negative $\mathbf{-174,3}\ ^{kJ}/_{mol}$ but minimized to $\mathbf{\Delta G_{eq2}}\ \mathbf{=}\Delta G_{min}\mathbf{=-90.4}\ ^{kJ}/_{mol}$ reached strong base equilibrium mixture $K_{eq2}\mathbf{=}10^{30,84}$**;**

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.

$[\mathbf{OH^-}]=[\mathbf{NH_4^+}]=C*\boldsymbol{\alpha}=0,001*0,1259=10^{-3,9}$ M$=1,259*10^{-4}$ M; $\boldsymbol{\alpha}=10^{-3,9}/0,001=0,1259$; 16th page

Dihydrogen phosphate $H_2PO_4^-{}_{aq}$ protolysis thermodynamic

CRC 2010 ; **BioThermodynamic2006** $H_2PO_4^-{}_{aq}+H_2O+\Delta G+Q\Rightarrow HPO_4^{2-}{}_{aq}+H_3O^+$ CRC2020;pH=7,36;

Substance	ΔH°_r, $^{kJ}/_{mol}$	ΔS°_r, $^{J}/_{mol/K}$	ΔG°_r , $^{kJ}/_{mol}$
H_3O^+	-285.81	-3.854	-213,275
H_2O	-285.85	69.9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$H_3PO_{4(aq)}$	-1271,7	150,8	-1123,6
$H_2PO_4^-$ (aq)	-1302,6	92.5	-1137,3
HPO_4^{2-} (aq)	-1292,14	-33,47	-1089,28
HPO_4^{2-} (aq)	**-1298,89**	**-810,792**	**-1057,143**
PO_4^{3-} (aq)	–1277,4	–220,5	–1018,7

1.$\Delta H_{Hess}=\Delta H^\circ_{products}-\Delta H^\circ_{reactants}$;2.$\Delta S_{Hess}=\Delta S^\circ_{products}-\Delta S^\circ_{reactants}$

CRC 2010; 3.$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

$=\mathbf{-1057{,}143}-213{,}275-(-1137{,}3\mathbf{-151{,}549})=\mathbf{18{,}43}$ $^{kJ}/_{mol}$

BioTherm2006;$\Delta G_H=\Delta G^\circ_{HPO42-}+\Delta G^\circ_{H3O}-\Delta G^\circ_{H2PO4-}-\Delta G^\circ_{H2O}=$

$=-1089{,}28-213{,}275-(-1137{,}3-237{,}191)=71{,}936$ $^{kJ}/_{mol}$

$\Delta H_H=\Delta H^\circ_{HPO42-}+\Delta H^\circ_{H3O}-\Delta H^\circ_{H2PO4-}-\Delta H^\circ_{H2O}=10{,}5$ $^{kJ}/_{mol}$ endot

$=-1292{,}14-285{,}81-(-1302{,}6-285{,}85)=10{,}5$ $^{kJ}/_{mol}$

2.$\Delta S_{disperse}=-\Delta H_H/T=-10{,}52/298{,}15=-35{,}3$ $^{J}/_{(mol\ K)}$;

3. $\Delta S_{total}=\Delta S_H+\Delta S_{disperse}=-199{,}784-35{,}3=-234{,}984$ $^{J}/_{(mol\ K)}$;

2. $\Delta S_H=\Delta S^\circ_{HPO42-}+\Delta S^\circ_{H3O}-\Delta S^\circ_{H2PO4-}-\Delta S^\circ_{H2O}=-33{,}47-3{,}854-(92{,}5+69{,}96)=-199{,}784$ $^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H=10{,}5-298{,}15*-0{,}199784=70{,}0$ $^{kJ}/_{mol}$; $=\mathbf{4{,}55}-298{,}15*\mathbf{-0{,}454}=\mathbf{140}$ $^{kJ}/_{mol}$ endoergic...

3. $T\bullet\Delta S_{total}=-234{,}984$ $^{J}/_{mol/K}$ $\bullet 298{,}15$ K= -70,0....$^{kJ}/_{mol}$ bound TΔSn accumulated energy.non **spontaneous**

Equilibrium reached by free energy minimum at compounds mixture ratio in expression of Prigogine attractor

equilibrium mixture: $\frac{[HPO_4^{2-}]_{aqua}\cdot[H_3O^+]}{[H_2PO_4^-]_{aqua}\cdot[H_2O]}=\mathbf{K_{eq2}}=\mathbf{K}_{H2PO4-}/[H_2O]=10^{-7{,}199}/55{,}3457339=1{,}143*10^{-9}$; $pK_{a2}=7{,}199$

$\mathbf{\Delta G_{eq2}=-R\bullet T\bullet ln(K_{eq2})}=-8{,}3144\bullet 298{,}15\bullet\mathbf{ln}(1{,}143*10^{-9})=51{,}04$ $^{kJ}/_{mol}$;

Dihydrogenphosphate $H_2PO_4^-{}_{aq}$ weqk acid $pK_a=7{,}199$ unfavored $H_2PO_4^-+H_2O\Rightarrow HPO_4^{2-}+H_3O^+$.

$\mathbf{K_a}=\frac{[HPO_4^{2-}]_{aqua}\cdot[H_3O^+]}{[H_2PO_4^-]_{aqua}}=[H_2O]\ \mathbf{K_{eq}}=55{,}3*1{,}144*10^{-9}=10^{-7{,}199}=10^{-pKa}$; $pK_a=7{,}199$;

$HPO_4^{2-}+H_2O\Rightarrow PO_4^{3-}{}_{aq}+H_3O^+=\mathbf{K_{eq3}}=\mathbf{K}_{HPO42-}/[H_2O]=10^{-12{,}35}/55{,}3457339=8{,}07*10^{-15}$; $pK_{a3}=12{,}35$

$\Delta G_H=\Delta G^\circ_{PO43-}+\Delta G^\circ_{H3O}-\Delta G^\circ_{HPO42-}-\Delta G^\circ_{H2O}=94{,}5$ $^{kJ}/_{mol}$;$=-1018{,}7-213{,}275-(-1089{,}28-237{,}191)=94{,}5$ $^{kJ}/_{mol}$;

$\mathbf{\Delta G_{eq3}=-R\bullet T\bullet ln(K_{eq3})}=-8{,}3144\bullet 298{,}15\bullet\mathbf{ln}(8{,}07*10^{-15})=80{,}44$ $^{kJ}/_{mol}$,

$H_3PO_4{}_{aq}+H_2O\Rightarrow H_2PO_4^-{}_{aq}+H_3O^+$; $\mathbf{K_{eq1}}=\mathbf{K}_{H3PO4}/[H_2O]=10^{-2{,}147975}/55{,}3457339=7{,}113*10^{-3}$; $pK_{a1}=2{,}148$

$\Delta G_H=\Delta G^\circ_{H2PO4-}+\Delta G^\circ_{H3O}-\Delta G^\circ_{H3PO4}-\Delta G^\circ_{H2O}=58{,}24$ $^{kJ}/_{mol}$;$=-1089{,}28-213{,}275-(-1123{,}6-237{,}191)=58{,}24$ $^{kJ}/_{mol}$;

$\mathbf{\Delta G_{eq1}=-R\bullet T\bullet ln(K_{eq1})}=-8{,}3144\bullet 298{,}15\bullet\mathbf{ln}(0{,}0001285)=22{,}21$ $^{kJ}/_{mol}$;

Endothermic and endoergic HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4 protolytic reaction free energy change $\mathbf{\Delta G_{protolyse}}$ positive 94,5 and 70,0 and 58,24 $^{kJ}/_{mol}$, but minimizes up to $\mathbf{\Delta G_{min}}=\mathbf{\Delta G_{eq}}=80{,}44$ and 51,04 and 22,21 $^{kJ}/_{mol}$ reaching equilibrium

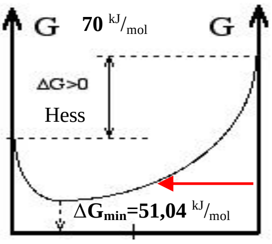
$HPO_4^{2-}{}_{aq}+H_2O\Rightarrow PO_4^{3-}{}_{aq}+H_3O^+$; $H_2PO_4^-+H_2O\Rightarrow HPO_4^{2-}+H_3O^+$;

$H_3PO_{4aq}+H_2O\Rightarrow H_2PO_4^-{}_{aq}+H_3O^+$; $pK_{a3}=12{,}35$, $pK_{a2}=7{,}199$, $pK_{a1}=2{,}148$

$$\frac{[H_2PO_4^-]_{aqua}\cdot[H_3O^+]}{[H_3PO_4]_{aqua}\cdot[H_2O]}=\mathbf{K_{eq1}}=\mathbf{K}_{H3PO4}/[H_2O]=10^{-2{,}148}/55{,}3=0{,}0001285;$$

$\mathbf{\Delta G_{eq3}=-R\bullet T\bullet ln(K_{eq3})}=-8{,}3144\bullet 298{,}15\bullet\mathbf{ln}(7{,}113*10^{-3})=80{,}44$ $^{kJ}/_{mol}$,

$$\frac{[PO_4^{3-}]_{aqua}\cdot[H_3O^+]}{[HPO_4^{2-}]_{aqua}\cdot[H_2O]}=\mathbf{K_{eq3}}=\mathbf{K}_{HPO42-}/[H_2O]=10^{-12{,}35}/55{,}3=8{,}07*10^{-15};$$



A+B 50% C+D

$H_2PO_4^-{}_{aq}+H_2O$

reactants products

$HPO_4^{2-}{}_{aq}+H_3O^+$.

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.

17th page

Enzyme CA Carbonic Anhydrase $\mathbf{CO_{2aqua}}$+$\mathbf{2H_2O}$ protolysis $\mathbf{2H_2O^{/CA/}CO_2/H_3O^+ + HCO_3^-}$ thermodynamics

$\mathbf{CO_2\uparrow_{gas}}$ no act $\mathbf{H_2O}$ just water soluble. Solubility in water $\mathbf{CO_2\uparrow_{gas}}$ **+ΔG** <=> $\mathbf{CO_{2aqua}}$**+Q exothermic**................

Substance	$\Delta H°_{Hess}$, $^{kJ}/_{mol}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$	$\Delta G°_{Hess}$, $^{kJ}/_{mol}$
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,274599
$\mathbf{OH^-}$	-230,015	-10,9	-157,2
$\mathbf{HCO_3^-}$	-689,93	98,324	-586,93988
$\mathbf{HCO_3^-}$	**-692,4948**	**-494,768**	**-544,9688**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{CO_{2aqua}}$	-413,7976	117,5704	-385,98
$\mathbf{CO_2\uparrow_{gas}}$	-393,509	213,74	-394,359

$\Delta H_H = \Delta H°_{CO2aq} - \Delta H°_{CO2gas} = -413.7976+393,509 = -20,3\ ^{kJ}/_{mol}$

$\Delta S_{Hess} = \Delta S°_{CO2aqua} - \Delta S°_{CO2gas} = 117,57-213,74 = -96,17\ ^{J}/_{mol/K}$;

$=117,57+69,9565-(213,74+69,9565) = -96,17$....... $^{J}/_{mol/K}$

$\Delta G_H = \Delta H_H - T*\Delta S_H = -20,3+298,15*0,09617 = 8,385\ ^{kJ}/_{mol}$;

$\Delta G_{sp} = \Delta G°_{CO2aq} - \Delta G°_{CO2gas} = -385,98+394,359 = 8,379\ ^{kJ}/_{mol}$

$K_{sp} = EXP(-\Delta G_{eq}/R/T) = EXP(-8379/8,3144/298,15) = 0,034045$

$$K_{sp}=0,0341=\frac{X^{CO_2 aqua}}{[CO_2\ gas]}=\frac{[CO_2\ aqua]}{[CO_2\ gas]\cdot[H_2O]}$$ 100% mol fraction

$[CO_{2gas}]=1$; $[CO_{2aqua}] = K_{sp}[H_2O] = 0,034*55,346 = 1,88$ M

Air 0,04% $[CO_{2gas}]=0,0004$; $[CO_{2aqua}] = K_{sp}*[CO_2\uparrow_{gas}]*[H_2O] = 0,034045*0,0004*55,3457339 = 0,000754$ M;

Hydrolysis reaction $\mathbf{CO_{2aqua}+2H_2O}$**+ΔG+Q** $\xrightarrow{CA}$ $\mathbf{H_3O^+ + HCO_3^-}$ and acid/base equilibrium

$\Delta H_H = \Delta H°_{H3O} + \Delta H°_{HCO3} - 2\Delta H°_{H2O} - \Delta H°_{CO2} = -285.81-689.93-(2*-285.85-413.7976) = 9.7576$.......... $^{kJ}/_{mol}$;

$\Delta S_{dispersed} = -\Delta H_{Hess}/T = -9,7576/298,15 = -32.727$....... $^{J}/_{mol/K}$; **endothermic**........................

2. $\Delta S_{Hess} = \Delta S°_{H3O} + \Delta S°_{HCO3} - 2\Delta S°_{H2O} - \Delta S°_{CO2} = -3,854+98,324-(2*69,9565+117,5704) = -163.0134$.......... $^{J}/_{mol/K}$;

$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = -32.727 -163.0134 = -195.169$........ $^{J}/_{mol/K}$;

3. $\Delta G_{Hess} = \Delta H_{Hess} - T*\Delta S_{Hess} = +9.7576+298.15*0.1630134 = 58.19$........... $^{kJ}/_{mol}$;

$T\bullet\Delta S_{total} = -195.7404{}^{*}298,15\ K = \mathbf{-58.19}$.......... $^{kJ}/_{mol}$; bound TΔSn← <u>accumulated free energy</u> **endoergic**...........

3. $\Delta G_{Hess} = \Delta G°_{H3O} + \Delta G°_{HCO3} - 2\Delta G°_{H2O} - \Delta G°_{CO2} = -213,2746\mathbf{-544,9688}-(2*-237,191-385,98) = 102\ ^{kJ}/_{mol}$;

Thermodynamic unfavored $$\frac{[HCO_3^-]aqua\cdot[H_3O^+]}{[CO_2]\ aqua\cdot[H_2O]^2} = \mathbf{K_{eq}} = \mathbf{K_{HCO3}} / [\mathbf{H_2O}]^2 = 10^{-7,0512} / 55,3^2 = 2,906*10^{-11}$$

$$\Delta \mathbf{G_{eq}} = \mathbf{-R\bullet T\bullet ln(K_{eq})} = -8,3144\bullet 298,15\bullet \mathbf{ln}(2,906*10^{-11}) = 60\ ^{kJ}/_{mol},$$

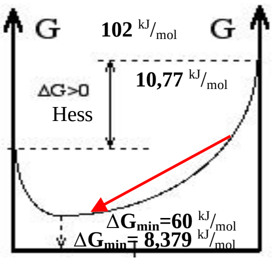
Endoergic $\mathbf{CO_{2gas}}$ solubility and $\mathbf{CO_{2aq}}$ protolysis Hess free energy change positive $\Delta \mathbf{G_{hydratation}} = 10,77.\ ^{kJ}/_{mol}$ and $\Delta \mathbf{G_{protolysis}}$ 102 $^{kJ}/_{mol}$, but minimizes reaching mixture solubility $\Delta \mathbf{G_{min}} = \Delta \mathbf{G_{sp}} = 8,379\ ^{kJ}/_{mol}$ and protolysis $\Delta \mathbf{G_{min}} = \Delta \mathbf{G_{eq}} = 60\ ^{kJ}/_{mol}$

Multiplication with water constant concentration $[\mathbf{H_2O}]^2 = 55,3^2\ ^{mol}/_{litrā}$;

$$K_{eq}=\frac{[HCO_3^-]aqua\cdot[H_3O^+]}{[CO_2]\ aqua\cdot[H_2O]^2} = \mathbf{2,91*10^{-11}};\ K_{CA} = K_{eq}\mathbf{*}[H_2O]^{\mathbf{2}} = \frac{[HCO_3^-]aqua\cdot[H_3O^+]}{[CO_2]\ aqua} = 10^{-7,0512}$$

Value $pK_{CA}=7,0512$ is frendly to physiologic pH=7,36 . Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

Reaction with hydroxide anion $\mathbf{CO_{2aqua}}$+ $\mathbf{OH^-}$**+ΔG+Q** <=> $\mathbf{HCO_3^-}$ is slow.



A+2B 50% C+D
$\mathbf{CO_{2aqua}+2H_2O}$
reactants produkti
$HCO_3^-+\mathbf{H_3O^+}$

$\Delta H_{Hess} = \Delta H°_{HCO3} - \Delta H°_{CO2} - \Delta H°_{OH} = -689,93-(-413,7976-230,015) = -46,1174$.......... $^{kJ}/_{mol}$;

exothermic........................

$\Delta S_{dispersed} = -\Delta H_{Hess}/T = 46,1174 /298,15 = 154,68\ ^{J}/_{mol/K}$; $\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = 154,68-8,3464 = 146,3336\ ^{J}/_{mol/K}$;

2. $\Delta S_{Hess} = \Delta S°_{HCO3} - \Delta S°_{CO2} - \Delta S°_{OH} = 98,324-(117,5704-10,9) = -8,3464$........... $^{J}/_{mol/K}$

3. $\Delta G_{Hess} = \Delta H_{Hess} - T*\Delta S_{Hess} = -46,1174-298,15*-0,0083464 = -43,63$........ $^{kJ}/_{mol}$;

$T\bullet\Delta S_{total} = 146,3336{}^{*}298,15\ K = \mathbf{43,63}$.......... $^{kJ}/_{mol}$; bound TΔSn← <u>accumulated free energy</u> **endoergic**...........

3. $\Delta G_{Hess} = \Delta G°_{HCO3} - \Delta G°_{CO2} - \Delta G°_{OH} = \mathbf{-544,9688}-(-385,98-157,2) = -1,7888\ ^{kJ}/_{mol}$; pH=7,36

$\mathbf{K_{OHess}} = EXP(-\Delta G_r /R/T) = EXP(1788,8/8,3144/298,15) = EXP(0,7216) = 2,058$; pH=7,36; pOH=6,64

$$\mathbf{K_{eqOH}}=\frac{[HCO_3^-]}{[CO_2]\ aqua\cdot[OH^-]} = \mathbf{K_{eq}/K_{H2O}} = 8914110,43\ ;\ \mathbf{K_{eqOH}}[\mathbf{OH^-}] = 8914110,43*10^{-6,64} = \frac{[HCO_3^-]}{[CO_2]\ aqua} = 2,042105;$$

$[\mathbf{HCO_3^-}] = \mathbf{K_{eq}}[\mathbf{OH^-}]*[\mathbf{CO_{2aqua}}] = 2,042105*0,00075125 = 0,0015341$ M;

Sum is $[\mathbf{CO_{2aqua}}]+[\mathbf{HCO_3^-}] = 0,00075125+0,0015341 = 0,0022854$ M 4th, 45th, 46th pages:

Note: pH=7,36 is Prigogine attractor to what tend organisms in homeostasis.

Sodium hydroxide solubility reaction with water $\mathbf{NaOH}+6\ \mathbf{H_2O} <=>[\mathbf{Na}<=(:\mathbf{OH_2})_6]^+ + \mathbf{OH^-} + \mathbf{Q}+\Delta G$;

100 $^{g}/_{100g}$ solubility in 200 g water solution of density 1,5217 $^{g}/_{mL}$; w%=50 %

$M_{NaOH}=\mathbf{Na}+\mathbf{O}+\mathbf{H}=23+16+1=40$.$^{g}/_{mol}$; $n_{NaOH}=m_{NaOH}/M_{NaOH}=760,85/40=19,02$ mol;
$n_{H2O}=m\ _{H2O}/M_{H2O}=760,85/18=42,27$ mol; nc=42,27/9=4,697 M; Double water mols number are enough for sodium ions coordination . Hydroxide ions repuls from water molecules stai alone.

Substance	$\Delta H°_H,^{kJ}/_{mol}$	$\Delta S°_H,^{J}/_{mol/K}$	$\Delta G°_H,^{kJ}/_{mol}$
$NaOH_{aq}$	-44,51	solution-	-
$NaOH.H_2O$	-21,41	solution	-
$NaOH_{lattic}$	-	lattice	-887
$NaOH_{Cryst}$	-425,8	64,4	-379,7
H_2O	-285.85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
H_3O^+	-285,81	-3,854	-
$Na+_{aqua}$	-240,10	59,00	-261,9
OH^-	-230.00	-10,539	-157,2

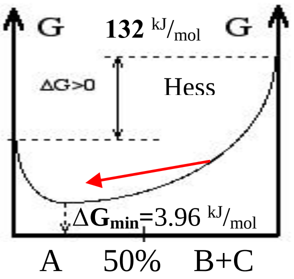
$\Delta H_{Hes}=\Delta H°_{Na}+\Delta H°_{OH}-\Delta H°_{NaOH}-2*\Delta H°_{H2O}=527,4\ ^{kJ}/_{mol}$;
$=-240,1-230-(-425,8-2*285.85)=527,4\ ^{kJ}/_{mol}$;
$\Delta S_{dispersed}=-\Delta H_H/T=-527,4/298,15= -1768,908\ ^{J}/_{(mol\ K)}$
$\Delta S_H=\Delta S°_{Na}+\Delta S°_{OH}-\Delta S°_{NaOH}-2*\Delta H°_{H2O}=59-10.539-64,4-2*69,9565=-155,852\ ^{J}/_{mol/K}$;
$\Delta S_{total}= \Delta S_{Hess}+ \Delta S_{dispersed}=-155,852-1768,908=-1924,76\ ^{J}/_{mol/K}$
$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=527,4-298,15*-0,155852=573,867\ ^{kJ}/_{mol}$;
$T\bullet\Delta S_{total}=-1,92476*298,15=$ **-573,867** $^{kJ}/_{mol}$ bound <u>free energy</u>
$\Delta G_H=\Delta G°_{Na}+\Delta G°_{OH}-\Delta G°_{NaOH}=467,9\ ^{kJ}/_{mol}$. **exoergic**.
$=-261,9-157,2-(-887)=467,9\ ^{kJ}/_{mol}$
Non dissociated hydroxide neutral molecules not forming:

I) Crystalline $\mathbf{Na^+OH^-}$ sodium hydroxide complete dissociates into ions coordinates two water $\mathbf{H_2O}$ w%=50 %.
$2\mathbf{Na^+OH^-}+(\mathbf{H_2O})_4=>2[2\mathbf{H_2O:=>Na^+}]_{aqua}+2\mathbf{OH^-}$; solubility constant is ions factorial at equilibrium:
Crystal sodium hydroxide dissociation solubility product: $\mathbf{Na^+OH^-}+2\mathbf{H_2O}=>[1.0469\mathbf{H_2O:=>Na^+}]_{aqua}+\mathbf{OH^-}$**;**
$\Delta G_{Hess}=\Delta G°_{Na}+\Delta G°_{OH}-\Delta G°_{NaOH}-2*\Delta G°_{H2O}=-261,9-157,2-(-379,7-2*237,191)=435\ ^{kJ}/_{mol}$;
Total concentration $n_{\mathbf{total}}$ $\mathbf{=[H_2O]+[[2H_2O:=>Na^+]_{aqua}]+[OH^-]}=4,23+19,02+19,02=\mathbf{42.27}$ M;
Solubility product in mol fractions $\mathbf{K_{sp}}=[\mathbf{Na^+}_{aqua}]*[\mathbf{OH}^-]_{aqua}/[\mathbf{Na^+OH^-}]/n_{\mathbf{kopā}}$^2=19,02*19,02/1/**42,27**^2=**0,2025**.
$\mathbf{\Delta G_{min}}=\Delta\mathbf{G_{sp}=-R\bullet T\bullet ln(K_{sp})}=-8,3144*298,15*\mathbf{ln}(0,\mathbf{2025})=\mathbf{3,959}\ ^{kJ}/_{mol}$.

<u>Solubility</u> 100 $^{g}/_{100g}$ solution density 1,5217 $^{g}/_{mL}$; w%=50 %; One liter solution contain
$n\ _{NaOH} = m_{NaOH}/M_{NaOH} = 760,85/40 = 19,02$ mol; $n_{H2O} = m\ _{H2O}/M_{H2O} = 760,85/18 = 42,27$ mol;
Two 2 water molecules coordinates linear at $\mathbf{Na^+}$ ions, but $\mathbf{OH^-}$ions repel water.
Hess change positive $\Delta G_{Hess}=\Delta G_{NaOH}+\Delta G_{(H2O)4}/2+2*\Delta G_{[H2O:=>Na+]}=887+45-800=132\ ^{kJ}/_{mol}$ endoergic, but minimized in mixture reached solubility equilibrium: $\Delta G_{eq}=\Delta G_{sp}=-8,3144\bullet 298,15\bullet ln(0,\mathbf{2025})=\mathbf{3,959}\ ^{kJ}/_{mol}$.
Solubility equilibrium is Prigogine attractor free energy change minimum $\Delta\mathbf{G_{min}}$.
At free energy change minimum reaching establishes crystalline sodium hydroxide $\mathbf{Na^+OH^-}$ solubility equilibrium .

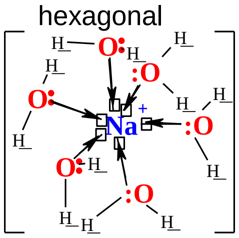
1. Ions lattice destruction: $\mathbf{NaOH=>Na^+ + OH^-}$ energy: $\Delta G_{NaOH}=887\ ^{kJ}/_{mol}$.
2. Tetra mer destruction: $(\mathbf{H_2O})_4=>4\mathbf{H_2O}$ energy $\Delta G_{(H2O)4}=90\ ^{kJ}/_{mol}$. w%=50 %

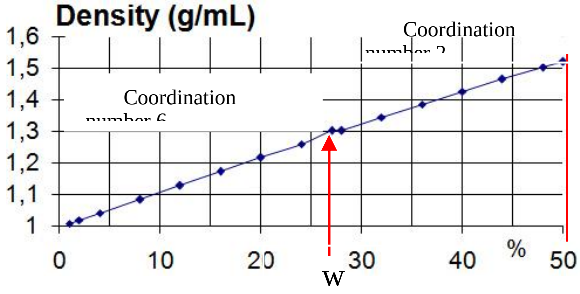
3.a Two $\mathbf{H_2O}$ coordination in cation energy $2*\Delta G_{[H2O:=>Na+]}=2*-400=-800\ ^{kJ}/_{mol}$:
$\Delta G_{Hess}=\Delta G_{NaOH}+\Delta G_{(H2O)4}/2+2*\Delta G_{[H2O:=>Na+]}=887+45-800=132\ ^{kJ}/_{mol}$.

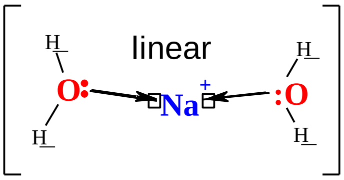


$\mathbf{Na^+OH^-}_{Cryst}=>$ products $\mathbf{Na^+ + OH^-}$

Notice: <u>Strong electrolytes</u> are soluble **exoergic** with negative $\Delta\mathbf{G}_{sp}\mathbf{<0}$ and greater one $\mathbf{K_{sp}>>1}$;
<u>Weak electrolytes</u> with positive $\Delta\mathbf{G}_{sp}\mathbf{>0}$ and 0 < $\mathbf{K_{sp} < 1}$ are <u>water insoluble</u> **endoergic**.
At 0% < w% < 27 % $\mathbf{NaOH}_{Cryst}$ solution density 1,301 $^{g}/_{mL}$ $2\mathbf{Na^+OH^-}+3(\mathbf{H_2O})_4=>2[6\mathbf{H_2O:=>Na^+}]_{aqua}+2\mathbf{OH^-}$;
3.b Six $\mathbf{H_2O}$ molecules coordinate symetrical around cation $6*\Delta G_{[H2O:=>Na+]}=6*-400=-2400\ ^{kJ}/_{mol}$:
$\Delta G_{reactions}=\Delta G_{NaOH}+3/2*\Delta G_{(H2O)4}+6*\Delta G_{[H2O:=>Na+]}=887+270/2-2400= -1378\ ^{kJ}/_{mol}$.







CALCULATION OF pH IN SOLUTIONS OF ACIDS AND BASES

In this chapter the formulae for pH calculation will be derived for the **4** most important cases in nature: weak and strong acid and base.

pH IN A SOLUTION OF STRONG ACID.

In a solution of strong acid the concentration of H_3O^+ ions can be calculated as $[H^+] = zC_{dis}$, where **z** is the number of H^+ ions in one molecule of acid, C_{dis} is the concentration of *dissociated* molecules.

As $C_{dis} = \alpha \cdot C_M$, the concentration of H^+ ions is $[H^+] = C_M \cdot \alpha \cdot z$ or, $C_M \cdot z = C_N$, $[H^+] = C_N \cdot \alpha$

Taking logarithm from both sides and changing signs we obtain: $pH = -\log [H^+] = -\log C_M \cdot \alpha \cdot z$.

pH in hydroxide solutions , strong base solution $pH = 14 - pOH = 14 + \log C_M \cdot \alpha \cdot z$

In hydroxide solutions $[OH^-]$ expression has the same form, as $[H^+]$ expression for strong acid: $[OH^-]=z \cdot C_{dis} = \alpha \cdot z \cdot C_M = \alpha \cdot C_N$. **pOH expression** as $-\log[OH^-]$, give for us: $pOH = -\log C_M \cdot \alpha \cdot z = -\log C_N \cdot \alpha$.

Classic WEAK ACID constant K_a *Ostwald's* dilution law

Two different characteristics for the protolysis of weak acids - the classic constant K_a and the dissociation degree α: $\alpha = n_{dis}/n_{total} = C_{dis}/C_{total}$.; $HB+H_2O=H_3O^+ + B^-$; $K_a=[H_3O^+] \cdot [B^-]/[HB]$ (**4.2**).

For calculations of protolytic products concentrations α is much more convenient, than K_a, because product concentrations can always be found as α product from the total acid+base concentration $C=[B^-]+[HB]$. Clearly α is not a constant value at: if the lower is the concentration of solution, the more easily protons escape from base and the lower is the probability to form back the acid. So, the lower is concentration **C**, the greater is α.

Dissociation constant, as all equilibrium constants, is not dependent on concentrations, as one value of dissociation constant at given temperature join K_a and α, expressing the protolysis products concentrations C_{dis} and insert the results into (**4.2**). Both products are equal and they are at the same dissociated amount concentration. Total concentration acid+base $C = [HB] + \alpha C$ of protolysis products $[H_3O^+]=[B^-]=C_{dis}=\alpha C$.

Concentration of non-dissociated molecules is equal to the difference between total the concentration of electrolyte and the concentration of dissociated molecules: $[HB] = C - C_{dis} = C - \alpha C$

Inserting all these results into (**4.2**) we have: $K_a = \dfrac{\alpha^2 C^2}{C - \alpha C} = \dfrac{\alpha^2 C}{1 - \alpha}$ Ostwald's dilution law **(4.4)**

Expression (**4.4**) in its present form allows the calculation of K_a, when α is known. The opposite case - calculation of α from known K_a is more common, therefore let us express α through K_a.

(**3**). As we are dealing with a weak electrolyte, $\alpha = 0$ and $(1 - \alpha)=1$ at the same time, therefore $K_a = \alpha^2 C$

and, solving it for α, we have $\alpha = \sqrt{\dfrac{K_a}{C}}$ **(4.4a)**

In (**4.4**a) it is seen mathematically, that the dilution is decrease the concentration of solution. Calculating the concentration of ions, we get: $[H_3O^+] = [B^-] = C_{dis} = \alpha C = C \cdot \sqrt{K_a / C} = \sqrt{K_a \bullet C}$

Weak acid hydrogen ions, hydroxonium concentration is: $[H_3O^+] = \sqrt{K_a \bullet C} = 10^{-pH}$ **Molarity**.

Weak acids high rate protolysis created attractor pH=7,36 keep irreversible Homeostasis. They are **CA** Carbonic Anhydrase bicarbonate acid form CO_{2aqua} , carbonic acids, amino acids, protonate amines, phospates:

Phosphates: $H_2PO_4^- + H_2O \Leftrightarrow H_3O^+ + HPO_4^{2-}$; $K_a = \dfrac{[H^+] \cdot [HPO_4^{2-}]}{[H_2PO_4^-]}$ $K_a = 6,3 * 10^{-8}$ M $= 10^{-7,199}$ M

Acetic acid: $CH_3COOH + H_2O \Leftrightarrow H_3O^+ + CH_3COO^-$; $K_a = \dfrac{[H^+] \cdot [CH_3COO^-]}{[CH_3COOH]_{nondis}}$ $K_a = 1,738 * 10^{-5}$ M $= 10^{-4,76}$ M

Protonate amonia: $NH_4^+ + H_2O \Leftrightarrow H_3O^+ + NH_{3\,aqua}$; $K_a = \dfrac{[NH_3]_{aqua} \cdot [H^+]}{[NH_4^+]_{aqua}}$ $K_a = [H_2O]^2 \dfrac{3.26 * 10^{-18}}{1,78 * 10^{-5}} = 10^{-9,25}$ M

[1]

In protein molecule work parallel protolytic equilibria. The average parallel equilibria pK_a constant value one calculates adding given N-terminus $pK_{a\text{-}NH3+}$ value, adding C-terminus $pK_{a\text{-}COOH^-}$ value and summing amino acids said chains $\Sigma pK_{aRgroup}$ values in total sum dividing with total count number NpK_a of functional groups :

pK_a=IEP=($\Sigma pK_{aRgroup}$+ $pK_{aNterminus}$+ $pK_{aCterminus}$)/NpK_a , where pK_a average is protein isoelectric point IEP as medium pH value having zero net charge of whole molekcule.

Amino acids **AA** have two types functional groups the carboxyl and the amino:

Amino acid **AA** carboxylic group protolytic pair acid **a**(*H_3CCOOH*) and conjugated base-salt **b**(*H_3CCOO^-*)

AA-COOH ⇔ **AA-COO**$^-$ + **H**$^+$, $pK_{aAACOOH}$< 4,5;

acid **a** ⇔ base **b** + **H**$^+$; attractor pH=7.36 in interval from 4.5 < 7.36 < 9,04

AA-NH_3^+ ⇔ **AA-N**H_2 + **H**$^+$, $pK_{aAANH3+}$> 9.04 ;

Protolytic pair acid **a**(**AA-N**H_3^+) protonated **N** and conjugated deprotonated **N** base **b** **AA-N**H_2 14th page:

$$K_{aCOOH}=\frac{[AA\text{-}COO^-]\cdot[H^+]}{[AA\text{-}COOH]_{nondis}}=10^{-pKa}\ ;\quad K_{aNH3+}=\frac{[AA\text{-}NH_2]\cdot[H^+]}{[AA\text{-}NH_3^+]_{protonated}}=10^{-pKa}\ ;$$

Like hemoglobin **Hb** proteins are long chain polypeptides of amino acids with four type protolytic acid groups:

Amino Acid	pK_{aCOOH}	pK_{aNH3+}	$pK_{aRgroup}$
Isoleucine	2.36	9.68	
Valine	2.32	9.62	
Leucine	2.36	9.60	
Phenylalanine	1.83	9.13	
Cysteine	1.96	10.28	8.18
Methionine	2.28	9.21	
Alanine	2.34	9.69	
Proline	1.99	10.96	
Glycine	2.34	9.60	
Threonine	2.11	9.62	
Serine	2.21	9.15	
Tryptophan	2.38	9.39	
Tyrosine	2.20	9.11	10.07
Histidine	1.82	9.17	6.00
Aspartate	1.88	9.60	3.65
Glutamate	2.19	9.67	4.25
Asparagine	2.02	8.80	
Glutamine	2.17	9.13	
Lysine	2.18	8.95	10.53
Arginine	2.17	9.04	12.48

-COO$^-$ deprotonated carboxyl negative anion salt groups, protonated positive charged ammonium groups **-N**H_3^+, neutral phenolic acid **–OH** and **-SH** neutral sulfhydryl groups.

In physiologic medium pH=7,36 ±0.01
Carbonic acid groups deprotonated negative charged **-COO**$^-$ and amino groups **R-N**H_3^+ protonated positive charged.
Table given maximal $pK_{a\text{-}COOH^-}$ value smaller about 7,36:
$pK_{a\text{-}COOH^-}$=4.25<7,36 and
given smallest $pK_{a\text{-}NH3+}$ value grater about 7,36 < 9,04 = $pK_{a\text{-}NH3+}$
20 amino acids have four protolytic pK_a equilibria in 47 groups:

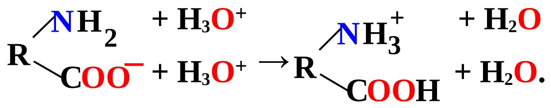
1. **R-COOH** ⇔**R-COO**$^-$ +**H**$^+$, 22 groups of 47
2. **R-N**H_3^+ ⇔**R-N**H_2 + **H**$^+$ 22+1 group of 47
3. **Tyrosine**-phenol-**OH**⇔**Tyrosine**-phenolate-**O**$^-$ +**H**$^+$ one group,
4. **Cysteine-SH** ⇔**Cysteine-S**$^-$ + **H**$^+$ one group .

NpK_a number of parallel protolytic equilibria average pK_a value is calculated as pK_a=(Σ $pK_{a\,R\,group}$+ $pK_{a\text{-}NH3+}$+ $pK_{a\text{-}COOH}$)/NpK_a

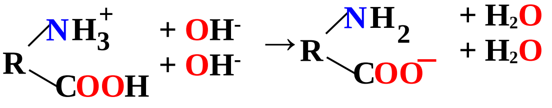
In *Ostwald's dilution law* calculates one the pH of solution at concentration C logarithm: $pH=\frac{pK_a-\log C}{2}$ =......

Histidine pK_{aNH3+}=6 do not have on protolysis influence at physiologic pH=7,36 .

If strong acid solution add to hemoglobin **Hb** like protein solution, than hydrogen **H_3O^+** ions react with deprotonated amino group and deprotonated carboxylate anion negative charged group.
Strong acid **H_3O^+** converts to water, neutralised **H_2O** .



If strong base add to protein solution, than hydroxyl **OH^-** ions react with weak acids ammonium group and carboxyl group.
Strong base **OH^-** converts to water, neutralised **H_2O**.



Molecules with multiple acid groups exist certain number **n** of parallel equilibria. Using mean value of pK_{mean} =(pK_1+pK_2+...+pK_n)/n is possible to calculate water medium pH value for molecule concentration **C** .

$pH=\frac{pK_{mean}-\log C}{2}$ and determination of molecule isoelectric point value pI=pK_{mean}.

For example: Average constant pK_{mean} for glycine solution **pH** with concentration C=0,100 mol/L!

Glycine average value pK_{mean}=(2,34+9,6+0)/2=5,97 and **pH**=$\frac{pK_{mean}-\log C}{2}=\frac{5{,}97+1}{2}$=3,485 !

Total concentration of multiple ions - *ionic strength* μ or I

CRC biochemistry Standard conditions since 2003th I=0,25 M , 0,1 M and pH=7,36

Many of the strong electrolytes (all water soluble salts, for instance) exist in an ionic crystalline already before dissolution. When they are dissolved in water, no dissociation is required - just ions are transferred from the crystalline into solution. From these considerations it is clear, that **α** = **1** in the solutions of strong electrolytes.

Crystalline $Na^{+}Cl^{-} + 12H_{2}O \uparrow => Na^{+} + 6H_{2}O + Cl^{-} + 6H_{2}O$

However, if **α** is measured experimentally (from the measurements of freezing point depression, boiling point raise, osmotic pressure or electrical conductivity of solution), the measured values of **α** are smaller than **1** - they often are around **α = 0.8-0.9**. As the true dissociation degree for the strong electrolytes is **1**. a conclusion has to be done, that only a part of ions is active, or, in other words, only a part (**0.8-0.9**) of ions express themselves in the properties of solution.

The reason of this is easily understood, if one considers the measurements of electrical conductivity. When electrodes are immersed into solution and a potential difference between them exists, positive ions should move towards the negative electrode and vice versa. Any positive ion is surrounded by negative ions, that make a *ionic atmosphere* around it. Forces of the electrical attraction from the side of ionic atmosphere work against motion of the ion towards the electrode, therefore the motion of ion in the electrical field is slower, than it could be, if ion was alone and the result of the conductivity measurement is lowered. For this reason, value of **α**, that is calculated from conductivity measurements, is lower than **1**.

It is easy to understand, that, the more dense is the ionic atmosphere, the smaller will be the measured **α**, which will be further called imaginary **α** (as the real **α** is equal to **1**).

$Na^{+}Cl^{-} + 12H_{2}O => [Na^{+}6H_{2}O]_{aqua} + (Cl^{-} + 6H_{2}O)$

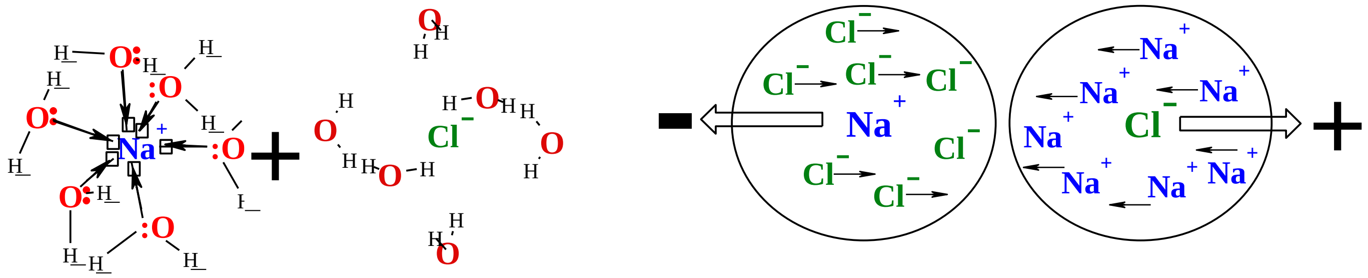


***Fig.4.1**. Ionic atmosphere around ions.*

The active concentration or *activity* of solute can be calculated from the total concentration of solute as

$$a = \gamma C, \text{ where } \gamma \text{ is the activity coefficient, } 0 < \gamma < 1.$$

Values of the activity coefficients can be calculated precisely from the expressions of *Debye - Hückels'* theory of strong electrolytes, but, as these expressions are very complicated, a more common case is to find of activity coefficients in tables.

As it can be understood from the previous material, the activity coefficient must be dependent on the density of ionic atmosphere - the more dense is the ionic atmosphere, the lower must be the activity coefficient. To characterize the density of ionic atmosphere a parameter, called *ionic strength* **μ** of solution is invented:

$$\mu = 1/2\ \Sigma\ C_{i} z_{i}^{2},$$

where C_i and z_i are the concentration and charge half sum **1/2 Σ** of each ion respectively.

Values of the activity coefficients are given in chemical tables for each given value of ionic strength.

Activity coefficient of a given ion depends on its charge, too. From fig.**4.1** it is easy to understand, that the greater is the charge of anion, the more it will be attracted by ionic atmosphere. For example, in a **0.01** M solution of Na_2SO_4 activity coefficients are γ_{Na+} = **0.85** for Na^+ ion and γ_{SO42-} = **0.45** for SO_4^{2-} ion.

2•**0.01** M + **0.01** M=0.03 Molarity is total concentration of ions for [Na_2SO_4] = **0.01** M.

$Na_2SO_4 => 2\ Na^+ + SO_4^{2-}$ and [Na^+]= 2•**0.01** M= 0.02 M, [SO_4^{2-}] = **0.01** M .

Electrolyte Na_2SO_4 ionic strength as total multiple ions concentration is:

$$\mu = ½(1^{2}•0.02+2^{2}•0.01) = = ½(1•0.02+4•0.01) = ½\ (0.02+0.04) = ½\ (0.06) = 0.03 \text{ Molarity}$$

THEORY OF pH INDICATORS

Indicators are compounds, which change their color according to the concentration of $\mathbf{H^+}$ ions in the solution. All the **pH** indicators themselves are weak acids or weak bases, the molecular form of which has a different color from the ionic form. Let us discuss indicator theory for a case, when the indicator is a weak acid (all conclusions will be the same in the opposite case, too **pOH value**). If we assign a symbol **HInd** to indicator, its dissociation process will be expressed by equilibrium, for example, to methyl orange:

$$\underset{red}{\mathbf{HInd}} \rightleftarrows \mathbf{H^+} + \underset{yellow}{\mathbf{Ind^-}}$$

Let us take as an example, that the **molecular form** of the indicator methyl orange has a color **red**, but the **ionic form** is **yellow**.

If the indicator is added to an acidic solution, the $\mathbf{H^+}$ ions of that solution will be involved in the equilibrium of indicator's dissociation and they will shift the equilibrium to the left. For this reason, the color of the molecular form will prevail and we shall see the solution in **red** color.

If the same indicator will be added to a basic solution, the $\mathbf{OH^-}$ ions from the solution will react with $\mathbf{H^+}$ ions from indicators equilibrium, the concentration of $\mathbf{H^+}$ will decrease and this will shift the equilibrium to the right. As a result, the ionic form of indicator will prevail in solution and we shall see the **solution yellow**.

The reason of color change is now clear, but it is necessary to know, at what value of **pH** each particular indicator will change its color. To find the **pH** interval of color change, we have to write an equation of equilibrium constant for indicator's dissociation and solve that equation against $\mathbf{[H^+]}$**:**

$$= \frac{+}{\qquad\qquad}$$

Expressing the concentration of hydrogen ions from the previous equation, we get:

$$\mathbf{[H^+] = K_{Ind}\frac{[HInd]}{[Ind^{\Box}]}}$$

and **pH** is obtained taking **log** from both sides of the equation using minus sign:

$$\mathbf{pH = \Box log[H^+] = \Box log K_{Ind}\frac{[HInd]}{[Ind^{\Box}]} = \Box log\, K_{Ind}\ \Box\, log\frac{[HInd]}{[Ind^{\Box}]}}$$

Taking into account, that **-logK=pK** and changing sign of the second part of the equation, **pH** becomes:

$$\mathbf{pH = pK_{Ind} + log\frac{[Ind^{\Box}]}{[HInd]}}$$

If the concentrations of both forms of indicator in the solution are equal, then

$$\mathbf{pH = pK_{Ind} + log1 = pK_{Ind} + 0 = pK_{Ind}}$$

The **pH** value, which is equal to $\mathbf{pK_{Ind}}$ of indicator is called the *color change point* of the indicator, as at this **pH** both forms are in equal amounts, but shifting **pH** to any side will cause domination of one form.

Visually indicator solution at $\mathbf{pH = pK_{Ind}}$ has an intermediate color (in our example - **orange color**).

The properties of the human eye are such, that it is possible to indicate visually the domination of one form, if its concentration is **10** times greater, than the concentration of the other form.

Thus, we will see the color of ionic form **yellow**, if the ratio $\frac{\qquad}{\qquad}$

$$\frac{\qquad}{\qquad} \quad \frac{\ }{\ }$$

and the color of molecular form **red**, if

Inserting the values **10** and **1/10** into the equation of **pH** we get the *color change interval* of the indicator:

$$\mathbf{pH = pK_{Ind} \pm 1}$$

(as **log 10 = 1** and **log 1/10 = -1**)

This means, that, using only one indicator, we can only say, whether **pH** is greater than $\mathbf{pK_{Ind}}$ + **1** (indicator will have the color of ionic form then) or it is below $\mathbf{pK_{Ind}}$ - **1** (indicator will have the color of **molecular form** then). Inside of the interval the indicator has an intermediate color and it is impossible to detect visually the dominance of any form.

CHOICE OF INDICATORS FOR ACID-BASE TITRATION

(see next chapter about hydrolysis if these questions are not clear)

At acid-base titration **pH** indicators are used to indicate the endpoint of titration. If a strong acid is titrated by a strong base (or vice versa), for example **HCl** is titrated by **NaOH:** $\mathbf{HCl + NaOH \Rightarrow NaCl + H_2O}$

At the endpoint of titration only **NaCl** and **water** are present in the solution. As **NaCl** is a salt of a strong acid and a strong base, it is not hydrolyzed and the solution is neutral, i.e. its **pH** = **7**. For this case of titration an indicator with $\mathbf{pK_{Ind}}$ value close to **7** will be required.
When a weak acid is titrated by a strong base, for example, acetic acid $\mathbf{pK_{CH_3COOH}}$=4,76 is titrated by **NaOH:**

$$\mathbf{CH_3COOH + NaOH \Rightarrow CH_3COONa + H_2O}$$

As sodium acetate is a salt of a weak acid, the anion $\mathbf{CH_3COO^-}$ is a rather strong base, therefore it is hydrolyzed as $\mathbf{pK_{CH_3COOH}}$ =4,76:

$$\mathbf{CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-}$$

As $\mathbf{OH^-}$ ions are formed in this equilibrium, the environment is basic and an indicator, having $\mathbf{pK_{Ind}}$ value greater than **7** approximately **10** is required, because $\mathbf{pOH_{hydrolyze}}=(\mathbf{14\ -\ 4{,}76\text{-}logC_{CH_3COONa}})/2=\mathbf{4}$, if $\mathbf{C_{CH_3COONa}}$ = **0,056 M .** When a weak base is titrated with a strong acid, e.g. $\mathbf{NH_3}$ is titrated by **HCl:**

$$\mathbf{NH_3 + HCl \Rightarrow NH_4Cl}$$

Weak acid $\mathbf{NH_4^+}$ react with base $\mathbf{H_2O}$ forming $\mathbf{NH_3}$ ammonia and hydrogen ion $\mathbf{H_3O^+}$
$\mathbf{NH_4^+ + H_2O \Rightarrow NH_3 + H_3O^+}$. Ammonium chloride water soluble forming up to 4,92 $^{mol}/_{L}$ ions $\mathbf{NH_4^+}$ concentration and due to $\mathbf{H_3O^+}$ ions salt solution is strong acid with **pH** <, **7** . (as is hydrolysed):

$$\mathbf{NH_4^+ + H_2O \Rightarrow NH_3 + H_3O^+}$$

$\mathbf{H^+}$ ions are a product of this equilibrium, therefore the environment is acidic and an indicator, having $\mathbf{pK_{Ind}}$ below **7** approximately **4** is required, because according Ostwald dilution law

$$\mathbf{pH_{hydrolyze}}=(\mathbf{9{,}25}+\mathbf{logC_{NH4}})/2=\mathbf{4},\ \text{if } \mathbf{C_{NH4}}=\ \mathbf{0{,}056\ M}.$$

VIII. HYDROLYSIS OF SALTS

Sam salt and **water** can be considered to be produced in a reaction between an acid and a base. As both of these two compounds can be strong or weak, there are **4** groups of salts:

1) SALT OF A STRONG ACID AND A STRONG BASE.

Salts of this group are not hydrolyzed, because anion of a strong acid is very weak base and metal ion of a strong base is a very weak acid.
Thus, for instance, $\mathbf{Na_2SO_4}$ is not hydrolyzed, as $\mathbf{SO_4^{2-}}$ ion is a very weak base and $\mathbf{Na^+}$ ion is a very weak acid.

2) SALT OF A WEAK ACID AND A STRONG BASE.

Let us take $\mathbf{Na_2CO_3}$ as example. In this case $\mathbf{Na^+}$ ion is not hydrolyzed, as it is a very weak acid, but $\mathbf{CO_3^{2-}}$ ion (as an anion of a weak acid) is a rather strong base and therefore it reacts with **water**. The hydrolysis of $\mathbf{CO_3^{2-}}$ ion occurs in **2** stages: *stage I:* $\mathbf{CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-}$

As $\mathbf{OH^-}$ ions are products of this equilibrium reaction, the environment in a solution of a salt of weak acid and strong base is basic, hence, its **pH** > **7**. stage II: $\mathbf{HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^-}$

Bicarbonate weak can be hydrolyzed further just with strong acid, as it can accept one more $\mathbf{H^+}$ ion, therefore stage II does not take a place with water: *stage II* **no reaction:** $\mathbf{HCO_3^- + H_2O = H_2CO_3 + OH^-}$

The second stage of hydrolysis, however, occurs to a very small extent. This can be explained by the following: $\mathbf{HCO_3^-}$ ion, which is the product of the first stage of hydrolysis, is the initial compound for the second stage. This means, that, when the **2**nd stage begins, there are already $\mathbf{OH^-}$ ions from the **1**st stage in the solution. If we consider the influence of the extra $\mathbf{OH^-}$ ions (from *stage I*) to the equilibrium of *stage II*, it is clear, that they shift the equilibrium to the left.

Thus, the **2**nd stage of hydrolysis is oppressed by the **1**st stage. For this reason, if we have to write the hydrolysis reaction in molecular form, we have to write it according to **1**st stage:

$$\mathbf{Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH}$$

For this group of salts, the hydrolysis will be increased by adding acid to solution (consider the influence of $\mathbf{H^+}$ on the equilibrium) and oppressed by adding base.

3) SALT OF A STRONG ACID AND A WEAK BASE, FOR EXAMPLE $ZnCl_2$.

In this case the anion is not hydrolyzed, as it comes from a strong acid and, hence, is a very weak base. The cation comes from a weak base and therefore it is a rather strong acid. It reacts with **water** (in this case, as Zn^{2+} is a bivalent ion, the hydrolysis reaction will again occur in **2** stages): *stage I:* $Zn^{2+} + H_2O \rightleftarrows ZnOH^+ + H^+$

As hydrogen ions are formed, the reaction of a solution of a salt of a strong acid and a weak base will be acidic, **pH** < **7**. *stage II:* $ZnOH^+$ ion can react with another molecule of **water**: $ZnOH^+ + H_2O \rightleftarrows Zn(OH)_2 + H^+$

Here the **2**nd stage of hydrolysis is oppressed by hydrogen ions from *stage I*, as they are already present in the solution when *stage II* begins. Thus, the molecular equation again has to be written for *stage I*:

$$ZnCl_2 + H_2O \rightleftarrows ZnOHCl + HCl$$

SPECIAL PROPERTIES OF SALTS WITH TRIVALENT METAL IONS

If the metal ion comes from a very weak trivalent base (for example, Bi^{3+}, Cr^{3+}, Sb^{3+}, Fe^{3+}), their hydrolysis really occurs up to the stage II (all together three stages could be possible in this case).

$$Bi^{3+} + H_2O \rightleftarrows BiOH^{2+} + H^+ \text{ ; } BiOH^{2+} + H_2O \rightleftarrows Bi(OH)_2^+ + H^+$$

and a molecule of H_2O is extracted from the product of *stage II*: $Bi(OH)_2^+ \Rightarrow BiO^+ + H_2O$.

The molecular form of the reaction has a form: $BiCl_3 + H_2O \rightleftarrows BiOCl + HCl$

The ions BiO^+, CrO^+, SbO^+ and FeO^+ are called *bismuthyl-*, *chromyl-*, *antimonyl-* and *ferryl-*ions respectively.

4) *salt of a weak acid and weak base*, for example CH_3COONH_4 or $(CH_3COO)_2Zn$.

In this case both ions are hydrolyzed, because the anion of a weak acid is a strong base and the metal ion of a weak base is a rather strong acid. For instance, for ammonium acetate we have to write hydrolysis equilibriums for both ions: $CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$; $NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$

In this case hydrolysis occurs to a great extent, because H^+ and OH^- ions, that are formed at the same time, combine together to form **water**: $H^+ + OH^- \Rightarrow H_2O$

As the concentration of a product of reaction drops down in both equilibriums, both equilibriums are shifted to the right.

To consider **pH** of the solution, one has to compare the strengths of acid and base, that have formed the salt. For example, for ammonium acetate, strength of acetic acid is equal to strength of ammonium hydroxide ($K_{CH_3COOH} = K_{NH_4OH} = 1.8\times10^{-5}$)

For this reason both acetate and ammonium ions are hydrolyzed to the same extent and the solution should be neutral, **pH** = **7**.

For zinc acetate the situation is different:

$Zn(OH)_2$ is much weaker as a base, than acetic acid as an acid. For this reason, zinc ion is more hydrolyzed, than acetate ion and the solution must be acidic (**pH** < **7**).

As it was shown a little before, a salt of a weak acid and a weak base is hydrolyzed to a great extent. If it happens so, that the salt is composed from a weak acid and a weak base and the final products of hydrolysis are gaseous, then the salt is completely decomposed by **water**. Such cases are: Al_2S_3, Cr_2S_3, $Al_2(CO_3)_3$, $Cr_2(CO_3)_3$ and $Fe_2(CO_3)_3$,

$$Al_2S_3 + 6H_2O \Rightarrow \underline{2Al(OH)}_3 + 3H_2S\uparrow$$

$$Cr_2S_3 + 6H_2O \Rightarrow \underline{2Cr(OH)}_3 + 3H_2S\uparrow$$

$$Cr_2(CO_3)_3 + 3H_2O \Rightarrow \underline{2Cr(OH)}_3 + 3CO_2\uparrow.$$

$$Fe_2(CO_3)_3 + 3H_2O \Rightarrow \underline{2Fe(OH)}_3 + 3CO_2\uparrow.$$

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