

In cell membrane compartments life solutions are equilibrium reaction products. Dissipative structure consisting

(membranes too) systems enzyme complexes driving irreversible processes to Prigogine **attractors** with Brownian molecular engines. Those are evolution and surviving instruments of homeostasis.

Nobel Prize in Chemistry 1977.

Solutions forming in favored and unfavored reactions with water reach Prigogine attractors

solubility product constant  $K_{sp}$  ,free energy change minimum  $\Delta G_{min}$  at equilibrium state.

In water dissolute oxygen  $O_2$  gas, carbon dioxide  $CO_2$  gas, hydrogen chloride  $HCl$  , ammonia (amines)  $NH_3$ .

In water dissolute crystalline salt sodium chloride  $NaCl_s$  , sodium acetate  $CH_3COONa_s$  ,

ammonium chloride  $NH_4Cl_s$  , sodium dihydrogen phosphate  $NaH_2PO_4$  , sodium hydrogen phosphate  $Na_2HPO_4$  ,

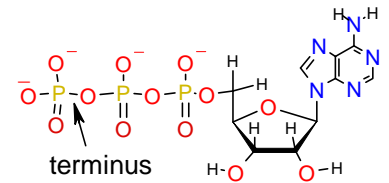
In water dissolute carboxylic acids, amino acids and amines as weak acids  $pK_a$  interval  $pH=2$  to  $10$ .

Weak acids a little react with water but balk consist

in protonate state like ammonium cations  $NH_4^+_{aq}$  and deprotonate state like :

deprotonate carboxylate  $-COO^-$  , deprotonate hydrogen  $HPO_4^{2-}$  phosphate and

deprotonate poly phosphate terminus like adenosine triphosphate  $ATP^{4-}$  ions



Protolytic equilibria undergoes at Biochemical conditions  $pH=7,36$ :

carboxylic, amino acids, protonate amines , proteins , digydrogen phosphates, terminus of poly phosphates.

Classic example is acetic acid  $CH_3COOH$  and ammonium ion  $NH_4^+_{aq}$  protolytic reaction with water and

Ostwald dilution law  $\alpha = \sqrt{\frac{K_a}{C}}$  for weak acetic acid :  $[H_3O^+] = \sqrt{K_a \cdot C} = 10^{-pH}$  Molarity

Oxygen no reaction with water as exist in triplet state inactive. **Triplet** oxygen atoms in molecule bound with three covalent bonds  $\cdot O \equiv O \cdot$ , however degenerate electron pair loosen another covalent orbital as radical, therefore in total **triplet** exhibit double bond in oxygen molecule  $:O=O:$  .

$O_{2,aqua}$  solution osmosis through aquaporin channels forms blood plasma  $O_{2,aqua-blood}$  solution .

Living organisms dissolute oxygen in osmosis through E7 class transport enzymes membrane aquaporins against concentration gradient forms normal concentration  $O_{2,aqu-Blood}$  isooxia. In blood plasma dissolute

$[O_{2,aqua}] = 9,768 \cdot 10^{-5}$  M if osmolar and ionic strength concentrations are  $C_{osm} = 0,305$  M,  $I = 0,25$  M,

but zero osmolar and ionic strength concentrations  $C_{osm} = 0$  and  $I = 0$  M as distilled water  $[O_{2,aq}] = 2,556 \cdot 10^{-4}$  M .

Osmolar, ionic strength, AIR oxygen physiologic concentration are  $C_{osm} = 0,305$  M,  $I = 0,25$  M,  $20,95\%$  .

Physiologic equilibrium constant  $K_{O_2Blood} = [O_{2,aqua}] / [O_{2,air}] = 9,768 \cdot 10^{-5} / 0,2095 = 4,663 \cdot 10^{-4} = 10^{-3,3314} = 10^{pK}$ .

Arterial blood concentration  $[O_{2,aqua}] = 6 \cdot 10^{-5}$  M and venous blood concentration is  $[O_{2,aqua}] = 1,85 \cdot 10^{-5}$  M.

<http://aris.gusc.lv/ChemFiles/ChromoHem/HbOxDeoxCO/HumanMeasure/O2Solutions.pdf>

Hyperoxia  $O_2$  excess rise oxidative stress, as non enzymatic oxidation destroy organism.

NASA Apollo project closed 1972 due to hyperoxia, because astronauts had to work in poor  $100\%$  oxygen atmosphere, that is five times greater about Earth atmosphere  $20,95\%$  oxygen. Such Hyperoxia is hazard nor for astronauts nor for NASA technologic Apollo equipment devices.

Hypoxia induce hypoxia induced factors cell proteins HIF, which work on nuclear receptors switch on in cells processes with decreased oxygen concentration - deficiency. Nobel Prize in Medicine 2019 .

ELSEVIER, Rotating Electrode Method and Oxygen reduction Electro catalysts, 2014, p.1-31,

Wei Xinga Min Yinb Qing Lvb Yang Hub Changpeng Liub Jiujun Zhangc: detect oxygen solubility.

Solubility at temperature  $25^\circ C$   $298,15 K$   $[O_{2,aqua}] = K_{O_2} = 1,22 \cdot 10^{-3}$  M, if  $100\%$  oxygen in AIR.

$$\text{Solubility constant } K_{eq} = \frac{[O_{2,aqua}]}{[O_{2,air}] \cdot [H_2O]} = K_{O_2} / [H_2O] = 1,22 \cdot 10^{-3} / 55,3 = 2,205 \cdot 10^{-5};$$

Poor 100% oxygen gas mol fraction is  $[O_{2, gas}] = 1$ . Atmosphere oxygen 20,95% mol fraction is 0,2095.

Solubility  $[O_{2, aqua}] = K_{O_2} = 1,22 \cdot 10^{-3} \text{ M} / 1 = \frac{[O_{2, aqua}]}{[O_{2, gas}]}$  is in water moles per litre mol/L over gas mol fractions 1.

Solubility from AIR 20,95%  $[O_{2, aqua}] = 1,22 \cdot 10^{-3} \cdot 0,2095 = 1,22 \cdot 10^{-3} \cdot 0,2095 = 2,556 \cdot 10^{-4} \text{ M}$ ;

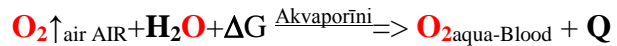
Mol fraction of water solution is ratio :  $[O_{2, aqua}] / [H_2O] = 1,22 \cdot 10^{-3} \text{ M} / 55,3 \text{ M} = K_{O_2} / [H_2O]$ .

Solubility product constant  $K_{eq} = \frac{[O_{2, aqua}]}{[O_{2, gas}] \cdot [H_2O]} = K_{O_2} / [H_2O] = 1,22 \cdot 10^{-3} / 55,3 = 2,205 \cdot 10^{-5}$ .....

$\Delta G_{min} = \Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(2,205 \cdot 10^{-5}) = -8,3144 \cdot 298,15 \cdot 6,414 = 26,58$ ..... kJ/mol;

Free energy **endoergic** change minimum value 26,58..... kJ/mol;!

Substance	$\Delta H_{Hess}^\circ$ kJ/mol	$\Delta S_{Hess}^\circ$ J/mol/K	$\Delta G_{Hess}^\circ$ kJ/mol
<b>O<sub>2</sub><sub>aqua</sub></b>	<b>-11,70</b>	<b>-94,2</b>	<b>16,40</b>
O <sub>2</sub> <sub>aqua</sub>	-11,715	110,876	16,4
O <sub>2</sub> ↑ <sub>gas</sub>	0	205,152	0
H <sub>3</sub> O <sup>+</sup>	-285,81	-3,854	-213,275
H <sub>2</sub> O	-285,85	69,9565	-237,191
<b>H<sub>2</sub>O</b>	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>



Biothermodynamic 2006; 1.  $\Delta H_{Hess} = \sum \Delta H^\circ_{products} - \sum \Delta H^\circ_{reactants}$

2.  $\Delta S_{Hess} = \sum \Delta S^\circ_{products} - \sum \Delta S^\circ_{reactants}$ ; 3.  $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess}$

$\Delta G_{Hess} = \Delta G^\circ_{H_2O} + \Delta G^\circ_{O_{2, aqua-Blood}} - \Delta G^\circ_{H_2O} - \Delta G^\circ_{O_{2, gas-AIR}} = \dots$  kJ/mol;

CRC 2010; = **16,4** - (-61,166) = **77,57** kJ/mol **endoergic**.....

1.  $\Delta H_{Hess} = \Delta H^\circ_{H_2O} + \Delta H^\circ_{O_{2, aqua-Blood}} - \Delta H^\circ_{H_2O} - \Delta H^\circ_{O_{2, gas-AIR}} = \dots$ , kJ/mol;

Biothermodyn 06; = **-11,7** (0,0) = **-11,7**..... kJ/mol **exothermic**.....

$\Delta S_{dispersed} = -\Delta H_{Hess} / T = 11,715 / 298,15 = \mathbf{39,292}$ ..... J/mol/K ;

$\Delta S_{Hess} = \Delta S^\circ_{H_2O} + \Delta S^\circ_{O_{2, aqua-Blood}} - \Delta S^\circ_{H_2O} - \Delta S^\circ_{O_{2, gas-AIR}} = -453,188 - 94,2 - (205,152 - 453,188) = -299,352$ ..... J/mol/K;

$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = -299,352 + 39,292 = -260,06$ ..... J/mol/K ;

3.  $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess} = -11,7 - 298,15 \cdot -0,299352 = \mathbf{77,55}$ ..... kJ/mol **endoergic**.....

$T \cdot \Delta S_{total} = -0,26006 \text{ kJ/K/mol} \cdot 298,15 \text{ K} = -77,5 \text{ kJ/mol}$ ; bound  $T \Delta S_{total} \leftarrow$  accumulate energy. unfavored **endoergic**;

Hess law calculation is exothermic and endoergic

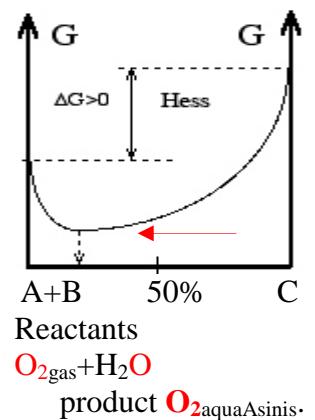
oxygen solubility havng free energy change positive

$\Delta G_{Hess} = 77,55$ ..... kJ/mol, but Prigogine attractor minimised unfavored equilibrium free energy change up to  $\Delta G_{min} = \Delta G_{eq} = 26,58$ ..... kJ/mol

reaching solubility equilibrium constant  $K_{eq} = \frac{[O_{2, aqua}]}{[O_{2, gas}] \cdot [H_2O]} = 2,205 \cdot 10^{-5}$ .....

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{min}$ .

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{min}$ .



$$\text{CO}_2 \text{ solubility constant } K_{\text{eq}} = \frac{[\text{CO}_2 \text{ aqua}]}{[\text{CO}_2 \text{ gas}] \cdot [\text{H}_2\text{O}]} = 1/29,44 \text{ and reaction with } \text{OH}^- \text{ ions.}$$

$\text{CO}_2 \uparrow_{\text{gas}}$  no reaction with water  $\text{H}_2\text{O}$  but dissolute with solubility constant  $K_{\text{eq}}=0,03397$ . (298.15 K).  
44<sup>th</sup> page: <http://aris.gusc.lv/BioThermodynamics/CO2O2Thermodynamic15A.pdf>

Substance	$\Delta H^\circ_{\text{H}}$ , kJ/mol	$\Delta S^\circ_{\text{H}}$ , J/mol/K	$\Delta G^\circ_{\text{H}}$ , kJ/mol
$\text{CO}_2 \uparrow_{\text{gas}}$	-393,509	213,74	-394,359
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191
$\text{H}_2\text{O}$	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>
$\text{CO}_2 \text{ aqua}$	-413,7976	117,5704	-385,98
$\text{H}_3\text{O}^+$	-230,00	-10,539	-157,2
$\text{H}_3\text{O}^+$	-285,81	-3,854	-213,2746
$\text{HCO}_3^-$	-689,93	98,324	-586,94
$\text{HCO}_3^-$	<b>-692,4948</b>	<b>-494,768</b>	<b>-544,9688</b>

$$\text{CO}_2 \text{ gas} + \text{H}_2\text{O} + \Delta G_{\text{stomata cell Membranes}} > \text{CO}_2 \text{ aqua} + \text{Q}$$

- $\Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$ ;  $3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$
- $\Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}$

$\Delta H_{\text{hydration}} = -17,9 \text{ kJ/mol}$ ;  **$\text{CO}_2$  hydration**  
 $\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{CO}_2 \text{ aqua}} - \Delta G^\circ_{\text{CO}_2 \text{ gas}} = +8,379 \text{ kJ/mol}$ ;  
 $\Delta G_{\text{Hess}} = -385,98 - (-394,359) = 8,379 \text{ kJ/mol}$  **endoergic**.....  
 1.  $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{CO}_2 \text{ aqua}} - \Delta H^\circ_{\text{CO}_2 \text{ gas}} = -20,2886 \text{ kJ/mol}$ ;  
 $\Delta H_{\text{Hess}} = -413,7976 - (-393,509) = -20,2886 \text{ kJ/mol}$  **exothermic**...  
 $\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}}/T = 20,2886/298,15 = 68,048 \text{ J/mol/K}$

$$\Delta S_{\text{dispersedHydration}} = -\Delta H_{\text{Hydration}}/T = 17,9/298,15 = 60,037 \text{ J/mol/K}$$

- $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{CO}_2 \text{ aqua}} - \Delta S^\circ_{\text{CO}_2 \text{ gas}} = 117,57 - (213,74) = -96,17 \text{ J/mol/K}$
- $\Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = -96,17 + 68,046 = -28,124 \text{ J/mol/K}$
- $\Delta S_{\text{total}} = \Delta S_{\text{Hydration}} + \Delta S_{\text{dispersedHydration}} = -96,17 + 60,037 = -36,13 \text{ J/mol/K}$

- $3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -20,1986 - 298,15 \cdot (-0,09617) = 8,3845 \text{ kJ/mol}$  **endoergic**.....
- $3. \Delta G_{\text{Hydration}} = \Delta H_{\text{Hydration}} - T \cdot \Delta S_{\text{Hess}} = -17,9 - 298,15 \cdot (-0,09617) = 10,77 \text{ kJ/mol}$  **Hydration**.....

$$T \cdot \Delta S_{\text{total}} = -28,124 \cdot 298,15 \text{ K} = -8,385 \text{ kJ/mol}; T \cdot \Delta S_{\text{total}} = -36,13 \cdot 298,15 \text{ K} = -10,77 \text{ kJ/mol}$$

$\text{CO}_2 \text{ aqua}$  reaction with hydroxide  $\text{OH}^-$  anions  $\text{CO}_2 \text{ aqua} + \text{OH}^- \Rightarrow \text{HCO}_3^- + \Delta G + \text{Q}$ ;  $\text{pOH}=5,9$  ocean;

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{HCO}_3^-} - \Delta G^\circ_{\text{CO}_2 \text{ aqua}} - \Delta G^\circ_{\text{OH}^-} = -586,94 - (-385,98 - 157,2) = -43,76 \text{ kJ/mol}$$
 **exoergic**.....  

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{HCO}_3^-} - \Delta H^\circ_{\text{CO}_2 \text{ aqua}} - \Delta H^\circ_{\text{OH}^-} = -689,93 - (-413,7976 - 230) = -46,1 \text{ kJ/mol}$$
 **exothermic**.....  

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{HCO}_3^-} - \Delta S^\circ_{\text{CO}_2 \text{ aqua}} - \Delta S^\circ_{\text{OH}^-} = 98,324 - (117,5704 - 10,539) = -8,7074 \text{ J/mol/K}$$
;  

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}}/T = 46,1324/298,15 = 154,73 \text{ J/mol/K}$$
;  

$$3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -46,1324 - 298,15 \cdot (-0,0087074) = -43,536 \text{ kJ/mol}$$
 **exoergic**.....  

$$K_{\text{OH}} = [\text{HCO}_3^-]/[\text{CO}_2 \text{ aqua}]/[\text{OH}^-] = \text{EXP}(-\Delta G_{\text{eq}}/R/T) = \text{EXP}(43760/8,3144/298,15) = 10^{7,6665} = 46395734$$
  

$$\Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = -8,7074 + 154,73 = 146 \text{ J/mol/K}$$
;  $T \cdot \Delta S_{\text{total}} = 146 \cdot 298,15 \text{ K} = 43,53 \text{ kJ/mol}$ ;

$$K_{\text{eqOH}} = \frac{[\text{HCO}_3^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2 \text{ aqua}] \cdot [\text{H}_2\text{O}]^2 \cdot [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]} = K_{\text{eq}}/K_{\text{H}_2\text{O}} = 2,906 \cdot 10^{-11}/3,26/10^{-18} = 8914110,43$$
 ; favored .

$$\Delta G_{\text{OH}} = -R \cdot T \cdot \ln(K_{\text{OH}}) = -8,3144 \cdot 298,15 \cdot \ln(8914110,42944785) = -39,67 \text{ kJ/mol}$$

Exothermic un exoergic water dissolute  $[\text{CO}_2 \text{ aqua}]$  Hess free energy change positive  $\Delta G_{\text{HessOH}} = -43,76 \text{ kJ/mol}$ , but minimised  $\Delta G_{\text{min}} = \Delta G_{\text{OH}} = -39,67 \text{ kJ/mol}$  reaching equilibrium  $k_{1 \rightarrow} / k_{2 \rightarrow} = K_{\text{OH}} = [\text{H}_2\text{O}][\text{HCO}_3^-]/[\text{CO}_2 \text{ aqua}][\text{OH}^-] = 8887917$  with ions  $\text{OH}^-$ .

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$ .

$$k'_{1 \rightarrow} = [\text{CO}_2 \text{ aqua}][\text{OH}^-] = 0,00056344 \cdot 10^{-5,9} (\text{pH}=8,1) = 10^{-9,149}$$
;  $k'_{2 \rightarrow} = [\text{HCO}_3^-] = 2,4 \cdot 10^{-3} \text{ M}$   

$$k'_{1 \rightarrow} = [\text{CO}_2 \text{ aqua}][\text{OH}^-] = 0,00075125 \cdot 10^{-5,9} (\text{pH}=8,1) = 10^{-9,02}$$
;  $k'_{2 \rightarrow} = [\text{HCO}_3^-] = 2,4 \cdot 10^{-3} \text{ M}$   
 Air 0,04% mol fraction  $[\text{CO}_2 \uparrow_{\text{air}}] = 0,0004$  as 400 ppm parts per million in atmosphere  
 dissolute:  $[\text{CO}_2 \text{ aqua}] = K_{\text{eq}} \cdot [\text{CO}_2 \uparrow_{\text{air}}] = 1,878 \cdot 0,0004 = 0,00075125 \text{ M}$ .

$$2020^{\text{th}} \text{ 0,04\% } K'_{\text{OH}0,04\%} = [\text{HCO}_3^-]/[\text{CO}_2 \text{ aqua}]/[\text{OH}^-] = 2,4 \cdot 10^{-3}/10^{-9,02} = 2513108,5$$

$$1989^{\text{th}} \text{ 0,03\% } K'_{\text{OH}0,03\%} = [\text{HCO}_3^-]/[\text{CO}_2 \text{ aqua}]/[\text{OH}^-] = 2,4 \cdot 10^{-3}/10^{-9,149} = 3382293 < K_{\text{eqOH}} = 8914110$$

Atmospheric  $\text{CO}_2$  shift  $K'_{\text{OH}0,04\%} = 2513108,5 < K'_{\text{OH}0,03\%} = 3382293 < K_{\text{OH}} = 8914110$  ocean equilibrium.

$$K_{\text{eqOH}} = \frac{[\text{HCO}_3^-]}{[\text{CO}_2]_{\text{ aqua}} \cdot [\text{OH}^-]} = K_{\text{eq}}/K_{\text{H}_2\text{O}} = 8914110,43$$
;  $K_{\text{eqOH}}[\text{OH}^-] = 8914110,43 \cdot 10^{-6,64} = \frac{[\text{HCO}_3^-]}{[\text{CO}_2]_{\text{ aqua}}} = 2,042105$ ;

$$[\text{HCO}_3^-] = K_{\text{eq}}[\text{OH}^-][\text{CO}_2 \text{ aqua}] = 2,042105 \cdot 0,00075125 = 0,0015341 \text{ M}$$
;

$$\text{Sum is } [\text{CO}_2 \text{ aqua}] + [\text{HCO}_3^-] = 0,00075125 + 0,0015341 = 0,0022854 \text{ M}$$

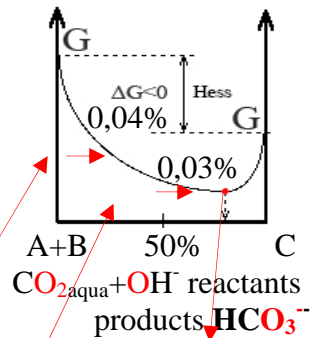
$$Q_{\text{total}} = Q_{\text{eq}} + Q_{\text{eqOH}} = -20,2886 + (-46,1) = -66,39 \text{ kJ/mol}$$
; exothermic;

$$\text{Reverse velocity } k_{1 \rightarrow} / k_{2 \rightarrow} = 1 \text{ equal to direct reaction } v_{2 \rightarrow} = k_{2 \rightarrow} [\text{HCO}_3^-] = 1 \cdot 2,4 \cdot 10^{-3} = 0,0024 \text{ M}^{-1} \text{ s}^{-1}$$
;

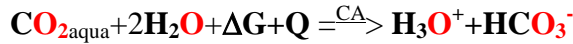
$$\text{Direct } v_{1 \rightarrow} = k_{1 \rightarrow} [\text{CO}_2 \uparrow_{\text{air}}][\text{OH}^-] = 1 \cdot 8914110,43 \cdot 0,004 \cdot 10^{-5,9} = 0,044889 \text{ M}^{-1} \text{ s}^{-1}$$
; 0,35656,  $\text{pOH}=5$ ; 3,5656,  $\text{pOH}=4$

$$\text{CA increase } [\text{CO}_2 \text{ aqua}] + [\text{HCO}_3^-] \text{ 30,6 times } v_{1 \rightarrow} = 30,6 \cdot 1 \cdot 8914110,43 \cdot 0,004 \cdot 10^{-5,9} = 1,37 \text{ M}^{-1} \text{ s}^{-1} \text{ versus } 0,00152$$

Limiting velocity diffusion in atmosphere, ocean. Acidifying per  $\Delta \text{pH} = -1$  decrease velocity and  $[\text{OH}^-]$  10 times.



E3 class enzyme hydrolase CA carbonic anhydrase drive carbon dioxide endothermic reaction with water



$$1. \Delta H_H = \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{HCO}_3^-} - 2\Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{CO}_2} = -285.81 - 689.93 - (2 \cdot -285.85 - 413.7976) = 9.7576 \dots \text{kJ/mol};$$

**Endothermic** hydroxonium and bicarbonate ions formation cool environment and is climate factor on Earth.

$$\Delta S_{\text{dispersed}} = -\Delta H_H / T = -9.7576 / 298.15 = -32.727 \dots \text{J/mol/K}.$$

$$2. \Delta S_H = \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{HCO}_3^-} - 2 \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{CO}_2} = -3.854 + 98.324 - (2 \cdot 69.9565 + 117.5704) = -163.0134 \dots \text{J/mol/K}$$

$$\Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{dispersed}} = -32.727 - 163.0134 = -195.7404 \dots \text{J/mol/K};$$

$$3. \Delta G_H = \Delta H_H - T \cdot \Delta S_H = 9.7576 + 298.15 \cdot 0.1630134 = 58.19 \dots \text{kJ/mol} \text{ endoergic} \dots$$

$$T \cdot \Delta S_{\text{total}} = -195.7404 \cdot 298.15 \text{ K} = -58.19 \dots \text{kJ/mol}; \text{ bound } T\Delta S \leftarrow \text{ saved free energy in products}.$$

$$3. \Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_3\text{O}^+} + \Delta G^\circ_{\text{HCO}_3^-} - 2\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{CO}_2} = -213,2746 - 544,9688 - (2 \cdot -237,191 - 385,98) = 102 \dots \text{kJ/mol};$$

Bicarbonate buffer systems  $\text{pK}_a = -\log K_{\text{HCO}_3} = \log(10^{-7.0512}) = 7.0512$  friendly to physiologic  $\text{pH} = 7.36$  and to

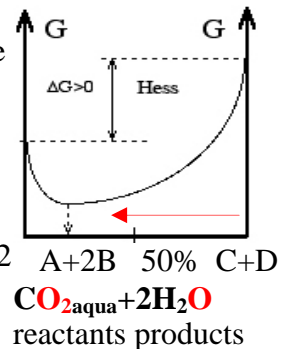
$$\text{Ratio in constant: } K_{\text{eq}} = \frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}} \cdot [\text{H}_2\text{O}]^2} = K_{\text{HCO}_3} / [\text{H}_2\text{O}]^2 = 10^{-7.0512} / 55.3^2 = 2,906 \cdot 10^{-11} \dots;$$

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

Endothermic and endoergic  $\text{CO}_{2\text{aq}}$  hydrolysis Hess free energy change  $\Delta G_{\text{hydrolysis}}$  positive 102  $\dots \text{kJ/mol}$ , but minimised in mixture  $\Delta G_{\text{eq}} = 60 \dots \text{kJ/mol}$  reaching

$$\text{equilibrium } K_{\text{eq}} = \frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}} \cdot [\text{H}_2\text{O}]^2} = 2,906 \cdot 10^{-11} \dots \text{Classic constant} :$$

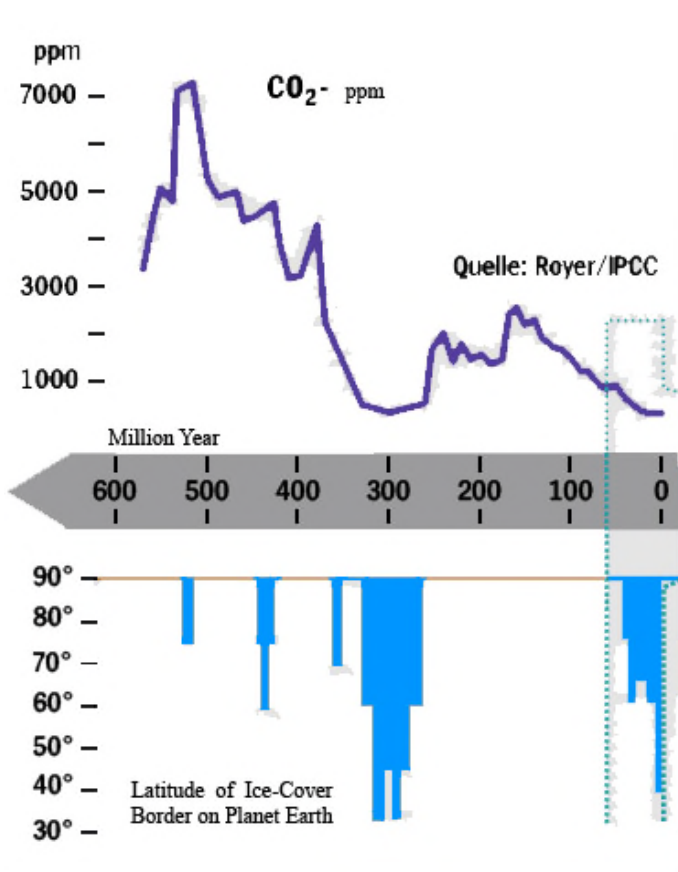
$$K_{\text{CA}} = K_{\text{eq}} \cdot [\text{H}_2\text{O}]^2 = 2,906 \cdot 10^{-11} \cdot 55,3^2 = \frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}} = 10^{-7.0512} \dots \text{pK}_{\text{CA}} = 7.0512$$



Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$ .

Free energy change minimum reaching establish equilibrium mixture.

$\text{pH} = 7.36$  Prigogine attractor to what tend homeostasis of organism. CA carbonic anhydrase drive irreversible  $\text{CO}_{2\text{aqua}} + 2\text{H}_2\text{O} + Q = 9,8 \text{ kJ/mol} \xrightarrow{\text{CA}} \text{H}_3\text{O}^+ + \text{HCO}_3^-$  carbon dioxide reaction with two water molecules. Planet cool CA and photosynthesis  $-20,95 \cdot 10^{17} \text{ kJ}$ . Warm 10 times less the reaction with  $\text{OH}^-$   $1,73 \cdot 10^{17} \text{ kJ}$   $2+4,55 \text{ Gt}$ .



Reconstruction climate of Earth shows temperature and  $\text{CO}_2$  oscillation, which 600 million years back in historical 10000 years period is observing Earth warming from  $-50^\circ$  to  $45^\circ$  degrees and carbon(IV) oxide gas concentration in air reaches 6%, what corresponds 60000 ppm. Climate changes are occurring with CA amount distinction 500 MY, 200 MY and new amounts of enzymes CA restoring 300 MY, 0-10 MY as decrease to days temperature and  $\text{CO}_2$  in ecosystem.

Before 600 million years  $\text{CO}_2$  concentration in atmosphere was 0.1% volume fractions, what agree 1000 ppm. Atmospheric oxygen  $\text{O}_2$  concentration approximately 1% from today's 20.95% volume fraction was unconformable for bulk of present-day animal species. Approximately 600 million years back Earth was ice covered reminding Snowball Earth. Glacier fast melting provokes  $\text{CO}_2$  concentration growth up to 6% 60000 ppm. Due to greenhouse effect temperature increases from  $-50^\circ$  up to  $45^\circ$  degrees, what because of photosynthetic reaction brought oxygen  $\text{O}_2$  concentration fast increase above present-day 20.95% up to 30%.

Prigogine attractor oxygen  $\text{O}_2$  20.95% concentration in air is working global for 500 million years.

Hydrogen chloride **HCl** solution and protolytic reareaction with water

Substance	$\Delta H^\circ_r, \text{kJ/mol}$	$\Delta S^\circ_r, \text{J/mol/K}$	$\Delta G^\circ_r, \text{kJ/mol}$
<b>Cl<sub>2</sub></b> <sub>aqua</sub>	-167,08	56,60	-
<b>H<sub>2</sub>O</b>	-285,85	69,956	-237,191
<b>H<sub>3</sub>O<sup>+</sup></b> <sub>(aq)</sub>	-285,81	-3,854	-213,275
<b>HCl</b> <sub>gas</sub>	-92,31	186,902	-95,3
<b>HCl</b> <sub>aqua</sub>	-167,2	56,5	-131,2

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$$1. \Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$$

$$2. \Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}; 3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}};$$



$$\Delta G^\circ_{\text{HClHess}} = -131,2 - (-95,3) = -36,59 \dots \text{kJ/mol}; \text{ exoergic} \dots$$

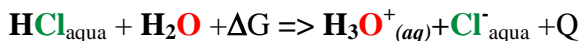
$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{HCl}_{\text{aqua}}} - \Delta S^\circ_{\text{HCl}_{\text{gas}}} = 56,5 - 186,902 = -130,402 \dots \text{J/mol/K};$$

$$1. \Delta H_{\text{Hess}} = \Delta H^\circ_{\text{HCl}_{\text{aqua}}} - \Delta H^\circ_{\text{HCl}_{\text{gas}}} = -167,2 - (-92,31) = -74,89 \dots \text{kJ/mol}.$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -74,89 - 298,15 \cdot (-0,130) = -36,01 \dots \text{kJ/mol} \text{ exoergic} \dots \text{exothermic} \dots$$

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}} / T = 74,89 / 298,15 = 251,182 \dots \text{J/mol/K}; T \cdot \Delta S_{\text{total}} = 120,78 \text{ J/K/mol} \cdot 298,15 \text{ K} = 36,01 \dots \text{kJ/mol};$$

$$3. \Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = 251,182 - 130,402 = 120,78 \dots \text{J/mol/K};$$



$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{Cl}^-} - \Delta H^\circ_{\text{HCl}_{\text{aq}}} - \Delta H^\circ_{\text{H}_2\text{O}} = -285,81 - 167,08 - (-167,2 - 285,85) = 0,16 \dots \text{kJ/mol}; \text{ athermic} \dots$$

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

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{Cl}^-} - \Delta S^\circ_{\text{HCl}} - \Delta S^\circ_{\text{H}_2\text{O}} = -3,854 + 56,60 - (69,956 + 56,5) = 52,64 - 126,46 = -73,714 \dots \text{J/mol/K}$$

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

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 0,16 - 298,15 \cdot (-0,073714) = 22,1378 \dots \text{kJ/mol} \text{ endoergic} \dots$$

$$T \cdot \Delta S_{\text{total}} = -74,251 \text{ J/K/mol} \cdot 298,15 \text{ K} = -22,14 \dots \text{kJ/mol};$$

37% Hydrochloric acid density 1,18 g/mL **HCl**<sub>aqua</sub> + **H<sub>2</sub>O** => **H<sub>3</sub>O<sup>+</sup>** + **Cl<sup>-</sup>** protolysis-dissociation constnt :

$$\frac{[\text{H}_3\text{O}^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{HCl}]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{dis}} = \exp(-\Delta G_{\text{Hess}} / R/T) = \exp(-22,1378291 / (8,3144 / 298,15)) = 1,323 \cdot 10^{-4} \dots$$

37% **HCl** mass in litre solution 1180 \* 0,37 = 436,6 .....g. Mols n<sub>HCl</sub> = 436,6 g / 36,45 = 11,978 .....mol

Water mass in litre solution m<sub>H<sub>2</sub>O</sub> = 1180 - 436,6 = 743,4 .....g. Number of mols n<sub>H<sub>2</sub>O</sub> = 743,4 / 18 = 41,3 .....mol

First solution: [H<sub>2</sub>O] = 41,3 - [H<sub>3</sub>O<sup>+</sup><sub>aq</sub>] = 41,3 - 0,25234 = 41,0477 ..... mol/L; C<sub>HCl</sub> = [HCl<sub>aqua</sub>] + [Cl<sup>-</sup>] = 11,98 .....M;

$$[\text{HCl}_{\text{aqua}}] = (11,978 - 0,252336) = 11,725664 \dots \text{mol/L};$$

$$[\text{HCl}_{\text{aqua}}] [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+_{\text{aq}}] \cdot [\text{Cl}^-_{\text{aqua}}];$$

As [Cl<sup>-</sup><sub>aqua</sub>] = [H<sub>3</sub>O<sup>+</sup><sub>aq</sub>] and replacing [Cl<sup>-</sup><sub>aqua</sub>] with [H<sub>3</sub>O<sup>+</sup><sub>aq</sub>] square equation is solved as: ax<sup>2</sup> + bx + c = 0 .

$$(11,7257 - [\text{Cl}^-]) [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+] \cdot [\text{Cl}^-_{\text{aqua}}]; (11,7257 - [\text{H}_3\text{O}^+]) [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{O}^+];$$

$$[\text{H}_3\text{O}^+]^2 + [\text{H}_2\text{O}] \cdot K_{\text{dis}} \cdot [\text{H}_3\text{O}^+] - K_{\text{dis}} \cdot [\text{H}_2\text{O}] \cdot 11,7257 = 0$$

Square equation ax<sup>2</sup> + bx + c = 0 solves real root of two mathematic x = 1 and 2

$$[\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+_{\text{aq}}] = \frac{-K_{\text{dis}} \cdot [\text{H}_2\text{O}] + \sqrt{(K_{\text{dis}} \cdot [\text{H}_2\text{O}])^2 - 4 \cdot (-K_{\text{dis}} \cdot [\text{H}_2\text{O}] \cdot 11,7257)}}{2} = 0,2523 \dots \text{M}$$

$$[\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+] = \left( \frac{-1,3293 \cdot 10^{-4} \cdot 41,0422 + \sqrt{(1,3293 \cdot 10^{-4} \cdot 41,0422)^2 - 4 \cdot (-1,3293 \cdot 10^{-4} \cdot 41,0422 \cdot 11,7257)}}{2} \right) = 0,2523 \dots \text{M}$$

Hydrogen ions concentration and pH in 37% hydrochloric acid solution:

$$[\text{H}_3\text{O}^+] = 0,2523 \dots \text{M} = 10^{-\text{pH}} = 10^{-0,598}; \text{pH} = -\log[\text{H}_3\text{O}^+_{\text{aq}}] = -\log 0,2523 = 0,598 \dots;$$

Dissociation degree  $\alpha = C_{\text{dis}} / C_{\text{M}} = 0,2523 / 11,978 = 0,02106 \dots$ ,  $\alpha\% = 2,106 \dots\%$

Equilibrium constane  $\frac{[\text{H}_3\text{O}^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{HCl}]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = (0,2523 \cdot 0,2523) / (41,0476 \cdot 11,725664) = 1,3293 \cdot 10^{-4} \dots$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,00013293) = 22,126 \dots \text{kJ/mol};$$

Unfavored protolysis Hess law positive: 22,14 .....kJ/mol, but minimised at equilibrium 22,126 .....kJ/mol .

Hydro chloric concentration is C<sub>HCl</sub> = [HCl<sub>aqua</sub>] + [Cl<sup>-</sup>] = 0,1 M ; [H<sub>2</sub>O] = 53,23 - [H<sub>3</sub>O<sup>+</sup><sub>aq</sub>] = 53,33 - 0,1 - 0,03 = 53,2 mol/L

$$[\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+] = \left( \frac{-1,323 \cdot 10^{-4} \cdot 53,2 + \sqrt{(1,323 \cdot 10^{-4} \cdot 53,2)^2 - 4 \cdot (-1,323 \cdot 10^{-4} \cdot 53,2 \cdot 0,1)}}{2} \right) = 0,03 \dots \text{M}$$

Equilibrium constant  $\frac{[\text{H}_3\text{O}^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{HCl}]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = (0,03 \cdot 0,03) / (53,2 \cdot 0,07) = 2,417 \cdot 10^{-4} \dots$

$$[\text{H}_3\text{O}^+] = 0,03 \dots \text{M} = 10^{-\text{pH}} = 10^{-1,52}; \text{pH} = -\log[\text{H}_3\text{O}^+_{\text{aq}}] = -\log 0,03 = 1,52 \dots;$$

Dissociation degree:  $\alpha = C_{\text{dis}} / C_{\text{M}} = 0,03 / 0,1 = 0,3 \dots$ ,  $\alpha\% = 30 \dots\%$

$\Delta G_{\text{Hess}} = 22,138 \dots \text{kJ/mol}$  endoergic ..... Prigogine minimum  $\Delta G_{\text{eq}} = 22,128 \dots \text{kJ/mol}$ ,

Ammonia  $\text{NH}_3\text{aq}$  solution and protonation and  $\text{NH}_4^+\text{aq}$  protolysis

16<sup>th</sup> page: <http://aris.gusc.lv/BioThermodynamics/CO2O2Thermodynamic15A.pdf>

1. Hydration;  $\text{NH}_3\text{gas} + \Delta G \Rightarrow \text{NH}_3\text{aq} + \text{Q}$ ;

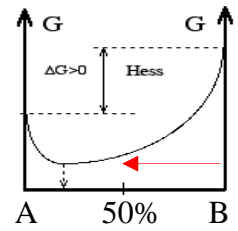
$$\Delta H_{\text{hydration}} = \Delta H^\circ_{\text{NH}_3\text{aq}} - \Delta H^\circ_{\text{NH}_3\text{gas}} = -132,5608 - (-45,94) = -86,6 \dots \text{kJ/mol};$$

$$\Delta G_{\text{Hydration}} = \Delta G^\circ_{\text{NH}_3\text{aq}} - \Delta G^\circ_{\text{NH}_3\text{gas}} = 91,1056 - (-16,4) = 107,5 \dots \text{kJ/mol};$$

$$\Delta S_{\text{Hydration}} = \Delta S^\circ_{\text{NH}_3\text{aq}} - \Delta S^\circ_{\text{NH}_3\text{gas}} = -739,2922 - 192,77 = -932,0622 \dots \text{J/mol/K};$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -86,6 - 298,15 \cdot (-0,9320622) = 191,3 \dots \text{kJ/mol};$$

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



izejviela  $\text{NH}_3\text{gas}$   
un products  $\text{NH}_3\text{aq}$

Ammonia  $\text{NH}_3\text{aq}$  protonation with water

2. Ammonia water strong base  $\text{NH}_3\text{aq} + \text{H}_2\text{O} + \text{Q} \Rightarrow \text{NH}_4^+\text{aq} + \text{OH}^- + \Delta G$  ammonium ion weak acid Brensted 1923.

1.  $\Delta H_{\text{H}} = \Delta H^\circ_{\text{NH}_4^+} + \Delta H^\circ_{\text{OH}^-} - \Delta H^\circ_{\text{NH}_3} - \Delta H^\circ_{\text{H}_2\text{O}} = -132,5608 - 286,65 - (-132,5 - 230,015) = -56,7 \dots \text{kJ/mol}$  **exothermic**

Substance	$\Delta H^\circ_{\text{H}}$ , kJ/mol	$\Delta S^\circ_{\text{H}}$ , J/mol/K	$\Delta G^\circ_{\text{H}}$ , kJ/mol
$\text{H}_3\text{O}^+$	-285,81	-3,854	-213,275
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191
$\text{H}_2\text{O}$	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>
$\text{NH}_4^+\text{aq}$	-132,5	113,4	-79,3
$\text{NH}_3\text{aq}$	<b>-132,5608</b>	<b>-739,2922</b>	<b>91,1056</b>
$\text{NH}_3\text{gas}$	-45,94	192,77	-16,4
$\text{OH}^-$	-230,015	-10,9	-157,2

1.  $\Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$ ; 3.  $\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$   
CRC 2010; 2.  $\Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}$

$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}}/T = 56,7/298,15 = 190,2 \dots \text{J/(mol K)}$

2.  $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_4^+} + \Delta S^\circ_{\text{OH}^-} - \Delta S^\circ_{\text{NH}_3} - \Delta S^\circ_{\text{H}_2\text{O}} = -1295 \dots \text{J/mol/K};$

$= 113,4 - 10,9 - (-739,2922 + 69,9565) = 771,8357 \dots \text{J/mol/K}$

3.  $\Delta S_{\text{total}} = \Delta S_{\text{H}} + \Delta S_{\text{dispersed}} = 190,159 + 771,8357 = 961,995 \dots \text{J/(mol K)}$ ;

$\Delta G_{\text{Hess}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -56,6958 - 298,15 \cdot 0,7718357 = -286,82 \dots \text{kJ/mol}$ .

$T \cdot \Delta S_{\text{total}} = 961,995 \cdot 298,15 = -286,8 \dots \text{kJ/mol}$ ; bound energy;

$\Delta G_{\text{min}} = \Delta G^\circ_{\text{NH}_4^+} + \Delta G^\circ_{\text{OH}^-} - \Delta G^\circ_{\text{NH}_3} - \Delta G^\circ_{\text{H}_2\text{O}} = -79,3 - 157,2 - (91,1056 - 151,549) = -176,06 \dots \text{kJ/mol}$  **exoergic**.....

$K_{\text{eq2}} = \exp(-\Delta G_{\text{Hess}}/R/T) = \exp(176056,6/8,3144/298,15) = 10^{30,84} \dots$ ; favored reaction strong base.

Hess change negative  $\Delta G_{\text{Hess}} = -286,82 \dots \text{kJ/mol}$  minimised at equilibrium mixture  $\Delta G_{\text{min}} = -176,06 \dots \text{kJ/mol}$ ;

3.  $K_{\text{eq3}}$ ; weak acid protolysis  $\text{NH}_4^+\text{aq} + \text{H}_2\text{O} + \Delta G + \text{Q} \Rightarrow \text{NH}_3\text{aq} + \text{H}_3\text{O}^+$ ;  $\text{NH}_4^+ = \text{H}^+ + \text{NH}_3\text{aq}$ ;  $\text{pK}_a = 9,25$ ;

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NH}_3} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{NH}_4^+} - \Delta G^\circ_{\text{H}_2\text{O}} = 91,1056 - 213,275 - (-79,3 - 151,549) = 108,68 \dots \text{kJ/mol}$  **endoergic**....

1.  $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NH}_3} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{NH}_4^+} - \Delta H^\circ_{\text{H}_2\text{O}} = -132,5 - 285,81 - (-132,5608 - 286,65) = 0,901 \dots \text{kJ/mol}$  **athermic**....

2.  $\Delta S_{\text{dispersed}} = -\Delta H_{\text{H}}/T = -0,901/298,15 = -3,02 \dots \text{J/(mol K)}$

2.  $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_3} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{NH}_4^+} - \Delta S^\circ_{\text{H}_2\text{O}} = -739,2922 - 3,854 - (113,4 - 453,188) = -403,4 \dots \text{J/mol/K}$

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 0,9008 - 298,15 \cdot (-0,4033582) = 121,2 \dots \text{kJ/mol}$  **endoergic**.....

$\Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = -3,021 - 403,358 = -406,4 \dots \text{J/(mol K)}$   $T \cdot \Delta S_{\text{total}} = -406,4 \cdot 298,15 = -121,2 \dots \text{kJ/mol}$ ;

$K_{\text{eq2}} = \frac{[\text{OH}^-]_{\text{aq}} \cdot [\text{NH}_4^+]_{\text{aq}}}{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = 10^{30,844} \dots$  strong base;  $K_{\text{eq3}} = \frac{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = 1,013 \cdot 10^{-11} \dots$  weak acid;

Classic constants ratio gain:  $K_{\text{eq3}} = [\text{H}_2\text{O}] \cdot K_{\text{H}_2\text{O}} / K_{\text{NH}_4\text{OH}} = [\text{H}_2\text{O}] \cdot \frac{3,26 \cdot 10^{-18}}{1,78 \cdot 10^{-5}} = 55,3 \cdot 1,831 \cdot 10^{-13} = 1,013 \cdot 10^{-11} \dots$

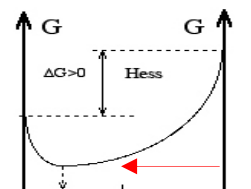
Classic weak acid constant value of Henderson Haselbalh equation  $\text{pH} = \text{pK}_a + \log(\frac{\text{nbāze}}{\text{nskābe}})$

$K_a = \frac{[\text{H}^+][\text{NH}_3]_{\text{aq}}}{[\text{NH}_4^+]_{\text{aq}}} = [\text{H}_2\text{O}] \cdot K_{\text{eq3}} = 55,3 \cdot 1,013 \cdot 10^{-11} = \dots = 5,6 \cdot 10^{-10} = 10^{-9,25} = 10^{-\text{pK}_a}$ ;  $\text{pK}_a = 9,25 \dots$ ;

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(1,013 \cdot 10^{-11}) = 62,76 \dots \text{kJ/mol}$ , Endothermic and exoergic  $\text{NH}_4^+\text{aq}$  protolysis Hess free energy change

$\Delta G_{\text{Hess}} = \Delta G_{\text{protolysis}} = 108,68 \dots \text{kJ/mol}$  is positive, but minimised to  $\Delta G_{\text{eq}} = 62,76 \dots \text{kJ/mol}$

reaching equilibrium mixture  $K_{\text{eq3}} = \frac{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = 1,013 \cdot 10^{-11} \dots$



A+B 50% C+D  
 $\text{NH}_4^+\text{aq} + \text{H}_2\text{O}$   
 $\text{NH}_3\text{aq} + \text{H}_3\text{O}^+$

Exothermic and exoergic  $\text{NH}_3\text{aq}$  and  $\text{H}_2\text{O}$  ionisation free energy change  $\Delta G_{\text{jonizācija}}$

negative  $-286,8 \dots \text{kJ/mol}$  but minimised to  $\Delta G_{\text{eq2}} = \Delta G_{\text{min}} = -176 \dots \text{kJ/mol}$

reaching strong base equilibrium mixture  $K_{\text{eq2}} = 10^{30,84} \dots$

Equilibrium reaching Prigogine attractor is free energy minimum  $\Delta G_{\text{min}}$ .

Free energy minimum reaching establishes equilibrium mixture.

$[\text{OH}^-] = [\text{NH}_4^+] = C \cdot \alpha = 0,001 \cdot 0,1259 = 10^{-3,9} \dots \text{M}$ ;  $\alpha = 10^{-3,9}/0,001 = 0,1259 \dots$ ; [ax2-bx-c-0NH4-CH3COO](#)

Sodium chloride NaCl **Solubility constant** and dissociation

10<sup>th</sup> page : <http://aris.gusc.lv/BioThermodynamics/CO2O2Thermodynamic15A.pdf>

**NaCl** Solubility 36 g/100g per hundred grams of water with **density** 1,203 g/mL ; w%=26,4706.....%

Litre solution mass with density 1,203 g/mL is  $m_{\text{solution}} = 1203 \dots \text{g/L}$ .

What times 136 g included in 1203 grams solution  $N_{\text{NaCl}} = 1203/136 = 8,8456 \dots$  times

$$m_{\text{NaCl}} = N_{\text{NaCl}} * 36 \text{ g/100g} = 8,8456 * 36 = 318,4416 \dots \text{g/L}$$

Molar mass **NaCl** is sum from atomic masses:  $M_{\text{NaCl}} = M_{\text{Na}} + M_{\text{Cl}} = 23 + 35,5 = 58,5 \dots \text{g/mol}$ .

Salt **NaCl** number of mols in litre is mass of saltj over it's molar mas:

$$n_{\text{NaCl}} = m_{\text{NaCl}} / M_{\text{NaCl}} = 318,4416 / 58,5 = 5,4434 \dots \text{mol/L} ; C_{\text{NaCl}} = 5,4434 \dots \text{mol/L} ;$$

Water  $m_{\text{H}_2\text{O}} = m_{\text{sk}} - m_{\text{NaCl}} = 318,4416 - 884,56 \dots \text{g} ; n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 884,558 / 18 = 49,142 \dots \text{mol}$ .

Mass fraction in percents is mass of salt over solution mass

$$m_{\text{NaCl}}/m_{\text{sk}} = 318,4416 / 1203 * 100\% = w\% = 26,4706 \dots \%$$

completely dissociate ions **crystalline NaCl** + Q =>  $\text{Na}^+_{\text{aqua}} + \text{Cl}^-_{\text{aqua}} + \Delta G$ ; solid, poor mol fraction is one

$[\text{Na}^+ \text{Cl}^-]_{\text{solid}} = 1$  and solubility product:  $K_{\text{spHess}} = [\text{Na}^+_{\text{aqua}}] * [\text{Cl}^-_{\text{aqua}}] = 5,4434 * 5,4434 = 29,6306 \dots$  is ions factorial, as Hess law reactant completely converts to products free energy change negative:

$$\Delta G_{\text{skHess}} = -R \cdot T \cdot \ln(K_{\text{skHess}}) = -8,3144 \cdot 298,15 \cdot \ln(29,6306) = -8,4 \dots \text{kJ/mol}$$

Non dissociate salt neutral molecules form in two ways: electrostatic and insufficient water coordination.

1. **Electrostatic** ions attraction *Debye - Hückels'* in 0,9 % physiologic solution forms osmolar  $C_{\text{osm}} = 0,305 \text{ M}$  concentration with sodium , chloride ions and salt neutral molecules :  $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$  in litre 1000 mL .

$C_{\text{osm}} = [\text{Na}^+] + [\text{Cl}^-] + [\text{NaCl}] = i * C_M = 0,305 \text{ M}$ . Isotonic coefficient  $i = 1 + \alpha \cdot (m-1)$ ;  $m = 1 + 1 = 2$  ions sum;

$$m_{\text{NaCl}}/m_{\text{solution}} = m_{\text{NaCl}} / 1000 * 100\% = w\% = 0,9\%$$
, because density is 1 g/mL .

$$. m_{\text{NaCl}} = 0,9\% * 1000 / 100\% = 9 \dots \text{g/L} ; n_{\text{NaCl}} = m_{\text{NaCl}} / M_{\text{NaCl}} = 9 / 58,5 = 0,15385 \dots \text{mol/L} ;$$

$$C_{\text{osm}} = [\text{Na}^+] + [\text{Cl}^-] + [\text{NaCl}] = i * C_M = (1 + \alpha(m-1)) * C_M = (1 + \alpha(2-1)) * 0,15385 = 0,305 \text{ M}$$

Disociation degree alpha shows non dissociate **[NaCl]** fraction concentration 0,0027 M:

$$\alpha = (0,305 / 0,15385 - 1) = 0,98245 . [\text{NaCl}] = C_M - C_M * \alpha = 0,15385 - 0,15385 * 0,98245 = 0,0027 \dots \text{M}$$

Physiologic solubility product is Prigogine attractor free energy minimum in 0,9% **NaCl** solution:

$$K_{\text{sp1}} = K_{\text{eq1}} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}] = 0,15115 * 0,15115 / 0,0027 = 8,4616 \dots ;$$

$$\Delta G_{\text{min1}} = \Delta G_{\text{sp1}} = -R \cdot T \cdot \ln(K_{\text{sp1}}) = -8,3144 \cdot 298,15 \cdot \ln(8,4616) = -5,294 \dots \text{kJ/mol}$$

Endothermic and exoergic solubility Hess free energy change  $\Delta G_{\text{Hess}} = -9,15 \dots \text{kJ/mol}$  is negative, but minimises  $\Delta G_{\text{min}} = \Delta G_{\text{sk1}} = -5,294 \dots \text{kJ/mol}$  in physiologic solution or in

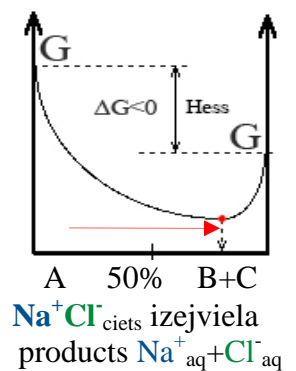
saturated solution  $\Delta G_{\text{sp2}} = -6,25 \dots \text{kJ/mol}$  reaching equilibrium mixture

$K_{\text{sp1}} = K_{\text{eq1}} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}] = 8,4616 \dots$  or  $K_{\text{sp2}} = K_{\text{eq2}} = 12,44 \dots$  in physiologic

0,9 % solution. Solubility equilibrium reach is Prigogine attractor free energy change

minimum  $\Delta G_{\text{min}}$  . Free energy minimum reaching established physiologic solution 0,9% or

**crystalline** sodium chloride  $\text{Na}^+ \text{Cl}^-$  **solubility product** equilibrium mixture.

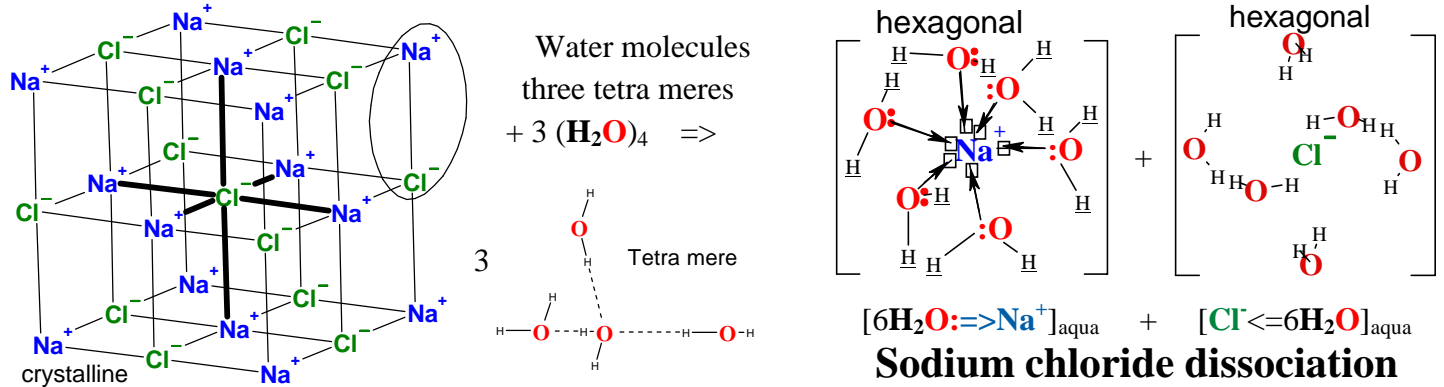


Note: Strong electrolytes are soluble with negative change  $\Delta G < 0$  and greater as one constant  $K_{\text{eq}} \gg 1$  ;

Weak electrolytes with positive change  $\Delta G_{\text{eq}} > 0$  and  $0 < K_{\text{eq}} < 1$  **endoergic** are slightly and like insoluble .

2. Second factor **coordination** around sodium and chloride ions indispensable use 12 water molecules:

$\text{Na}^+\text{Cl}^- + 8\text{H}_2\text{O} \Rightarrow [\text{6H}_2\text{O} \Rightarrow \text{Na}^+]_{\text{aqua}} + [\text{Cl}^- \Leftarrow \text{6H}_2\text{O}]_{\text{aqua}}$  water resources count  $n_c = 49,142/12 = 4,0952 \dots \text{M}$ .  
 $\text{Na}^+\text{Cl}^-$  dissipative disorder three tetra meres  $3(\text{H}_2\text{O})_4$  and ions coordinate six water molecules together 12:



Part **NaCl** remains non dissociate neutral molecules due to insufficient water resources 49,142 mols.

Saturated non dissociate  $[\text{NaCl}] = 5,4434 - 4,0952 = 1,3482 \dots \text{M}$ ; degree  $\alpha = 4,0952/5,4434 = 0,75 \dots 75,2 \%$

$$K_{sp2} = K_{eq2} = [\text{Na}^+_{\text{aq}}] \cdot [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}] = 4,0952 \cdot 4,0952 / 1,3482 = 12,4393 \dots$$

$$\Delta G_{sp2} = -R \cdot T \cdot \ln(K_{sp2}) = -8,3144 \cdot 298,15 \cdot \ln(12,4393) = -6,25 \dots \text{kJ/mol}$$

Substance	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
$\text{Na}^+\text{Cl}^-$	-411,12	72,00	-
$\text{Na}^+_{\text{aq}}$	-240,10	59,00	-
$\text{Cl}^-_{\text{aqua}}$	-167,2	56,50	-
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191
$\text{H}_2\text{O}$	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>
$\text{H}_3\text{O}^+$	-285,81	-3,854	-213,275

crystalline  $\text{Na}^+\text{Cl}^- + \text{Q} \Rightarrow \text{Na}^+_{\text{aqua}} + \text{Cl}^-_{\text{aqua}} + \Delta G$ ; **endothermic**.....

$$\Delta H_{\text{Hessa}} = \Delta H^\circ_{\text{Na}} + \Delta H^\circ_{\text{Cl}} - \Delta H^\circ_{\text{NaCl}} = -240,1 - 167,2 - (-411,12) = 3,82 \dots \text{kJ/mol}$$

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hesa}} / T = -3,82 / 298,15 = -12,812 \dots \text{J/(mol K)}$$

$$\Delta S_{\text{Hesa}} = \Delta S^\circ_{\text{Na}} + \Delta S^\circ_{\text{Cl}} - \Delta S^\circ_{\text{NaCl}} = 59 + 56,50 - (72) = +43,5 \dots \text{J/mol/K}$$

$$\Delta G_{\text{Hessa}} = \Delta H_{\text{Hessa}} - T \Delta S_{\text{Hessa}} = 3,82 - 298,15 \cdot 0,0435 = -9,15 \dots \text{kJ/mol}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{H}} + \Delta S_{\text{dispersed}} = -12,812 + 43,5 = +30,688 \dots \text{J/mol/K}$$

$$T \cdot \Delta S_{\text{total}} = 30,688 \cdot 298,15 = 9,15 \dots \text{kJ/mol bound lost free energy}$$

Diluted, physiologic solution coordination number is complete with  $\text{H}_2\text{O}$  molecules for  $\text{Na}^+$  and  $\text{Cl}^-$  ions 6.

1) **crystalline** sodium chloride  $\text{Na}^+\text{Cl}^-$  **separation** to  $\text{Na}^+$  cations and negative  $\text{Cl}^-$  anions,

2) Tetra mere  $(\text{H}_2\text{O})_4$  brake ions  $[\text{Na}(\text{H}_2\text{O})_6]^+$ ,  $[\text{Cl}(\text{H}_2\text{O})_6]^-$  **hydrate** with water molecules in coordination six.

**Crystalline** sodium chloride dissolute in water:



Solubility dissociation Hess free energy  $\Delta G = -9,15 \text{ kJ/mol}$

change negative dissipative split ions in **crystalline** and solubility process in **water** is spontaneous, favored.

Heat accumulates in products **endothermic**  $\Delta H_{\text{Hessa}} = +3,82 \text{ kJ/mol}$  with cooling. Heat dispersion negative

$\Delta S_{\text{izkriede}} = -12,812 \text{ J/(mol K)}$ , but hydration with chemical energy dispersion positive  $\Delta S_{\text{hidratatācijas}} = 43,5 \text{ J/(mol K)}$

Total entropy change is positive  $+30,688 \text{ J/(mol K)}$  dissipative separate **crystalline** in ions  $\text{Na}^+ + \text{Cl}^-$ .

Total  $\Delta H$  change two processes sum  $\Delta H_{\text{Hessa}} = \Delta H^{\text{separation}} + \Delta H^{\text{hydration}} = 3,82 \text{ kJ/mol}$  **endothermic** positive,

where  $\Delta H^{\text{separation}} > 0$  is positive heat supplied to separate ions positive from negative each from other. Bound

energy  $\Delta H^{\text{separation}} > 0$  is positive, but  $\Delta H^{\text{hydration}}$  in **hydration** process evolved heat **exothermic**  $\Delta H^{\text{hydration}} < 0$  is

negative and less by absolute value therefore total sum is positive 3,82. Sslt reaction with **water** is **endothermic**

$\Delta H_{\text{Hessa}} = 3,82 \text{ kJ/mol}$ . It applicate to melting ice mixture, that decrease temperature up to  $-12^\circ \text{C}$ . Freezing cause the

positive change  $\Delta H_{\text{Hessa}}$  value  $3,82 \text{ kJ/mol}$  in summary  $\Delta H^{\text{separation}} + \Delta H^{\text{hydration}}$ .





Ammonium chloride  $\text{NH}_4\text{Cl}_{(s)} \Rightarrow \text{NH}_4^+_{(aq)} + \text{Cl}^-_{\text{aqua}}$  water solution and dissociation

Data from tables: solubility  $39,5 \frac{\text{g}}{100\text{g H}_2\text{O}}$ , density  $1,3536 \frac{\text{g}}{\text{mL}}$ ,

Litre solution has with density  $1,3536 \frac{\text{g}}{\text{mL}}$  is  $m_{\text{solution}} = 1353,6 \dots\dots\dots \frac{\text{g}}{\text{L}}$ .

What times  $139,5 \text{ g}$  include  $1353,6 \text{ grams solution}$   $1353,6/139,5 = 9,7032 \dots\dots\dots$  times

Ammonium chloride mass in litre  $m_{\text{NH}_4\text{Cl}} = 9,7032 * 39,5 \text{ g} = 383,2764 \dots\dots\dots \frac{\text{g}}{\text{L}}$ .

Molar mass is sum of atomic masses:  $M_{\text{NH}_4\text{Cl}} = M_{\text{NH}_4} + M_{\text{Cl}} = 14 + 4 + 35,5 = 53,5 \dots\dots\dots \frac{\text{g}}{\text{mol}}$ .

Salt number of mols in litre is salt mass over its molar mass:

$$n_{\text{NH}_4\text{Cl}} = m_{\text{NH}_4\text{Cl}} / M_{\text{NH}_4\text{Cl}} = 383,2764 / 53,5 = 7,164 \dots\dots\dots \frac{\text{mol}}{\text{L}} ; C_{\text{NH}_4\text{Cl}} = 7,164 \dots\dots\dots \frac{\text{mol}}{\text{L}} ;$$

Water  $m_{\text{H}_2\text{O}} = m_{\text{sk}} - m_{\text{NH}_4\text{Cl}} = 1353,6 - 383,2764 = 970,32 \text{ g}$   $n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 970,32/18 = 53,907 \dots\dots\dots \text{moli}$ .

Mass ratio in percents is mass of salt over solution mass:

$$m_{\text{NH}_4\text{Cl}}/m_{\text{sk}} = 383,2764/1353,6 * 100\% = w\% = 28,32 \dots\dots\dots \%$$

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

Substance	$\Delta H^\circ_{\text{Hess}}$ , kJ/mol	$\Delta S^\circ_{\text{Hess}}$ , J/mol/K	$\Delta G^\circ_{\text{Hess}}$ , kJ/mol
$\text{Cl}^-_{\text{aqua}}$	-167,2	56,50	-
$\text{NH}_4^+_{(aq)}$	-132,5	113,4	-
$\text{NH}_4\text{Cl}_{(s)}$	-314,4	94,6	-202,97

reactants  $\text{NH}_4\text{Cl}_{(s)} + \text{Q} \Rightarrow \text{NH}_4^+_{(aq)} + \text{Cl}^-_{\text{aqua}} + \Delta G_{\text{products}}$

$$1. \Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{Reactants}} ;$$

$$2. \Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{Reactants}} ;$$

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

$$1. \Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NH}_4} + \Delta H^\circ_{\text{Cl}} - \Delta H^\circ_{\text{NH}_4\text{Cl}} = -132,5 - 167,2 - (-314,4) = -299,7 + 314,4 = 14,7 \dots\dots\dots \frac{\text{kJ}}{\text{mol}} \text{ endothermic} \dots\dots\dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}}/T = -14,7/298,15 = -49,3 \dots\dots\dots \frac{\text{J}}{\text{mol/K}} ;$$

$$2. \Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_4} + \Delta S^\circ_{\text{Cl}} - \Delta S^\circ_{\text{NH}_4\text{Cl}} = 113,4 + 56,50 - 94,6 = 169,9 - 94,6 = 75,3 \dots\dots\dots \frac{\text{J}}{\text{mol/K}}$$

$$3. \Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = -49,3 + 75,3 = 26 \dots\dots\dots \frac{\text{J}}{\text{mol/K}} ;$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 14,7 - 298,15 * 0,0753 = -7,75 \dots\dots\dots \frac{\text{kJ}}{\text{mol}} ; \text{ exoergic} \dots\dots\dots$$

$$T \cdot \Delta S_{\text{total}} = 26 \frac{\text{J}}{\text{K/mol}} \cdot 298,15 \text{ K} = 7,75 \dots\dots\dots \frac{\text{kJ}}{\text{mol}} ;$$

$$\frac{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{NH}_4\text{Cl}]_{\text{solid}}} = K_{\text{spHess}} = \exp(-\Delta G_{\text{Hess}}/R/T) = \exp(7,75/8,3144/298,15) = 22,8 \dots\dots\dots$$

Thermodynamic favored Hess solubility product in water.

Complete dissociation solubility product constant  $K_{\text{dis}} = [\text{NH}_4^+_{aq}] * [\text{Cl}^-_{\text{aqua}}] = 7,164 * 7,164 = 51,32 \dots\dots\dots$

Ammonium chloride  $K_{\text{dis}} = 22,8$  non dissociated concentration is calculated in expression:

$$[\text{NH}_4\text{Cl}_{\text{aqua}}] = [\text{NH}_4^+_{aq}] * [\text{Cl}^-_{\text{aqua}}] / K_{\text{spHess}} = 51,323/22,8 = 2,251 \dots\dots\dots \frac{\text{mol}}{\text{L}} ,$$

including equal dissociated ions concentration in subtraction solubility concentration minus non dissociated salt concentration:

$$[\text{NH}_4^+_{(aq)}] = [\text{Cl}^-_{\text{aqua}}] = 7,164 - 2,251 = 4,913 \dots\dots\dots \frac{\text{mol}}{\text{L}} ,$$

$$\text{Favored solubility product constant: } K_{\text{eq}} = \frac{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{NH}_4\text{Cl}]_{\text{aqua}}} = 4,913 * 4,913 / 2,251 = 10,723 \dots\dots\dots$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10,723) = -5,881 \dots\dots\dots \frac{\text{kJ}}{\text{mol}} ,$$

Endothermic and exoergic  $\text{NH}_4\text{Cl}_{(s)}$  dissociation Hess free energy change

$$\Delta G_{\text{Hess}} = \Delta G_{\text{dis}} = -7,75 \dots\dots\dots \frac{\text{kJ}}{\text{mol}} \text{ is negative, but minimized reaching}$$

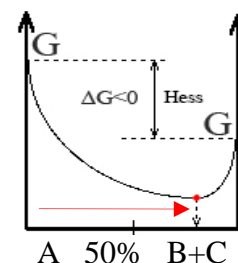
$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -5,881 \dots\dots\dots \frac{\text{kJ}}{\text{mol}}$$

$$\text{solubility equilibrium mixture } K_{\text{eq}} = \frac{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{NH}_4\text{Cl}]_{\text{aqua}}} = 10,723 \dots\dots\dots$$

reactant non dissociated ammonium chloride  $\text{NH}_4\text{Cl}_{\text{aqua}}$  A  
and products are ions  $\text{NH}_4^+_{\text{aqua}} + \text{Cl}^-_{\text{aqua}}$

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$ .

Free energy change minimum reaching establish equilibrium mixture.



Dihydrogen phosphate  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  salt solubility and protolytic pair reaction with water

$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  solubility 94,9 g/100g, density 1,32 g/mL; w%=73 g/194,9 g\*100%=37,455.....%;

Litre solution mass with density 1,32 g/mL is  $m_{\text{solution}} = 1320$  ..... g/L

What times 194,9 g include 1320 grams solution  $1320/194,9 = 6,7727$ .....times

Sodium dihydrogen phosphate mass in litre  $m_{\text{NaH}_2\text{PO}_4} = 6,7727 * 94,9 \text{ g} = 642,72923$ .....g/L..

$M_{\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}} = (M_{\text{Na}} + M_{\text{P}} + M_{\text{O}_4} + M_{\text{H}_2}) + M_{2\text{H}_2\text{O}} = (23 + 31 + 4 * 16 + 2) + 2 * 18 = 156 = 120$ .....g/mol + 36.....g/mol .

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

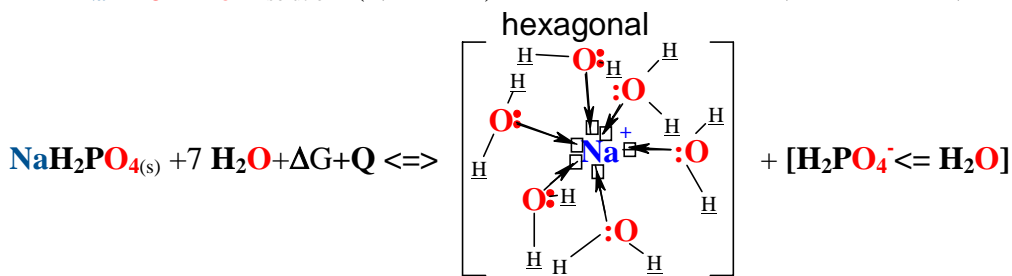
$n_{\text{NaH}_2\text{PO}_4} = m_{\text{NaH}_2\text{PO}_4} / M_{\text{NaH}_2\text{PO}_4} = 642,72923 / (120 + 36) = 4,12$ ..... mol/L ;  $C_{\text{NaH}_2\text{PO}_4} = 4,12$ ..... mol/L ;

Water  $m_{\text{H}_2\text{O}} = m_{\text{sk}} - m_{\text{NH}_4\text{Cl}} = 1320 - 642,73 + 4,12 * 36 = 825,6$  grams;  $n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 825,59 / 18 = 45,86$ .....mols.

Saturated solution water coordination resources 7 are enough :  $n_c = n_{\text{H}_2\text{O}} / 7 = 45,866 / 7 = 6,55231$ .....mol.

Mass fraction in percents dividing mass of salt with solution mass

$m_{\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}} / m_{\text{solution}} = (4,12 * 120) / 1320 * 100\% = w\% = 37,455$ .....%;



Thermodynamic favored Hess solubility in water.

Complete dissociated solubility constant is  $K_{\text{sp\_eq1}} = [\text{Na}^+_{\text{aq}}] * [\text{H}_2\text{PO}_4^-_{\text{aq}}] = 4,12 * 4,12 = 16,9744$ .....

$\Delta G_{\text{sp\_eq1}} = -R \cdot T \cdot \ln(K_{\text{sp\_eq1}}) = -8,3144 \cdot 298,15 \cdot \ln(16,9744) = -7,02$ ..... kJ/mol.

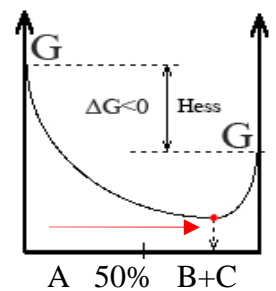
Coordination minimum with water 7 molecules resources 45,8667/7=6,55231 moils are enough for complete dissolve salt concentration 4,12 M coordination.

Exoergic  $\text{NaH}_2\text{PO}_4(s)$  solubility product constant reaction Hess free energy change

$\Delta G_{\text{sp\_Hess1}} = \text{?????}$ ..... kJ/mol negative (missing data about  $\text{NaH}_2\text{PO}_4(s)$ ), but minimised

$\Delta G_{\text{min}} = \Delta G_{\text{sp\_eq1}} = -7,02$ ..... kJ/mol in mixture reaching solubility product equilibrium

$K_{\text{sp\_eq1}} = [\text{Na}^+_{\text{aq}}] * [\text{H}_2\text{PO}_4^-_{\text{aq}}] / [\text{NaH}_2\text{PO}_4(s)] = 4,12 * 4,12 = 16,9744$ .....



In mixture is solid crystalline reactant

$\text{NaH}_2\text{PO}_4(s)$

and products

$\text{Na}^+_{\text{aq}} + \text{H}_2\text{PO}_4^-_{\text{aq}}$

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$  .

Free energy change minimum reaching establish equilibrium mixture.

Sodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4$  solubility product equilibrium and reaction with water

$$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} \quad 11,8 \text{ g}/100\text{g}, \text{ density } 1,045 \text{ g}/\text{mL}; \text{ w}\%=5,2452\text{.....}\%$$

Litre solution mass with density  $1,045 \text{ g}/\text{mL}$  is  $m_{\text{solution2}} = 1045 \text{ .....g}/\text{L}$ .

What times 111,8 g includes 1045 grams of solution  $1045/111,8 = 9,347\text{.....times}$

Sodium hydrogen phosphate mass in litre  $m_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} = 9,347 \cdot 11,8 \text{ g} = 110,2946\text{.....g}/\text{L}$ .

$$M_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} = (2M_{\text{Na}} + M_{\text{P}} + M_{\text{O}_4} + M_{\text{H}}) + 7 M_{\text{H}_2\text{O}} = (2 \cdot 23 + 31 + 4 \cdot 16 + 1) + 7 \cdot 18 = 142\text{.....g}/\text{mol} + 126\text{.....g}/\text{mol}$$

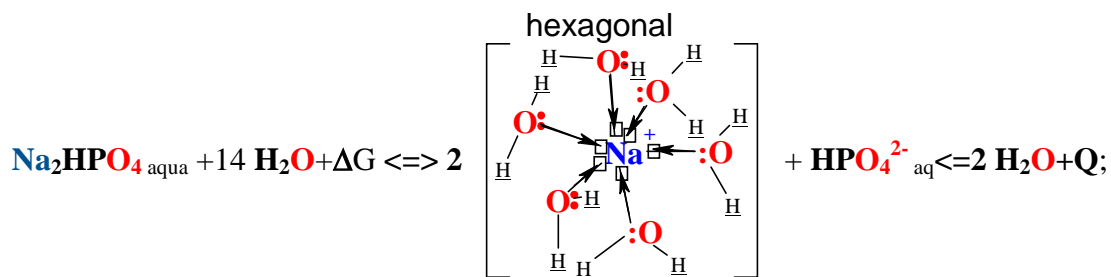
$$w_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} = 1,0000 = 0,5298507(\text{Na}_2\text{HPO}_4) + 0,470149254(7\text{H}_2\text{O})$$

Salt number of mols in litre is mass of salt over it's molar mass  $142 + 126 = 268\text{.....g}/\text{mol}$ :

$$n_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} = m_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} / M_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} = 110,2946 / 268 = 0,386 \text{ ..... mol}/\text{L}; C_{\text{Na}_2\text{HPO}_4} = 0,386\text{..... mol}/\text{L};$$

Water  $m_{\text{H}_2\text{O}} = 1045 - 0,386 \cdot 142 = 990,2\text{.....grams}$ ;  $n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = (1045 - 54,812) / 18 = 55,01\text{.....mols}$ ;

Mass fraction in percents :  $m_{\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}} / m_{\text{sk}} = 54,812 / 1045 \cdot 100\% = \text{w}\% = 5,2452\text{.....}\%$ ;



Thermodynamic  $\text{NaH}_2\text{PO}_4(\text{s})$  unfavored Hess solubility product in water.

Disociate solubility product constant is  $K_{\text{sp\_eq}} = [\text{Na}^+_{\text{aq}}]^2 \cdot [\text{HPO}_4^{2-}_{\text{aq}}] = 0,386^3 = 0,05751\text{.....}$

$$\Delta G_{\text{sp\_eq}} = -R \cdot T \cdot \ln(K_{\text{sp\_eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,05751) = 7,07934\text{..... kJ}/\text{mol}.$$

Indispensible coordinated water is 14 accessible in water resources  $55,01/14 = 3,9293\text{.....mols}$

water concentration is in excess for Hess complete conversion salt 0,386 M occupied:

Endoergics  $\text{NaH}_2\text{PO}_4(\text{s})$  solubility product reaction Hess free energy change

$\Delta G_{\text{spHess}} = +\text{?????}\text{..... kJ}/\text{mol}$  is positive (missing data about  $\text{Na}_2\text{HPO}_4(\text{s})$ ), but minimised

$\Delta G_{\text{min}} = \Delta G_{\text{sp\_eq}} = +7,07934\text{..... kJ}/\text{mol}$  in mixture

reaching dissociation equilibrium  $K_{\text{sp\_eq}} = [\text{Na}^+_{\text{aq}}]^2 \cdot [\text{HPO}_4^{2-}_{\text{aq}}] = 0,074837\text{.....}$

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$ .

Free energy change minimum reaching establish equilibrium mixture.

Apparent equilibrium constant  $\text{Na}_2\text{HPO}_4(\text{solid}) + \Delta G \rightleftharpoons 2 \text{Na}^+ + \text{HPO}_4^{2-}(\text{aq}) + \text{Q}$ ;

Three products concentration mol fraction over total sum

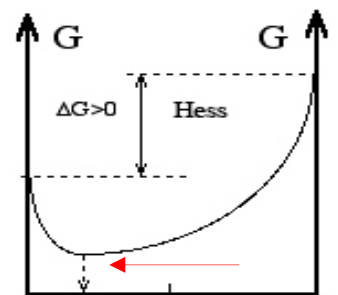
$$[\text{H}_2\text{O}] + 2 \cdot [\text{Na}^+] + [\text{HPO}_4^{2-}] = 55,01 + 3 \cdot 0,386 = 56,168\text{.....M}$$

$[\text{Na}^+] / [\text{H}_2\text{O}] = [\text{Na}^+] / 56,168$ ,  $[\text{H}_2\text{PO}_4^-] / [\text{H}_2\text{O}] = [\text{H}_2\text{PO}_4^-] / 56,168$ . Solid mol fraction

is one  $[\text{Na}_2\text{HPO}_4(\text{solid})] = 1$  and water mol fraction is  $[\text{H}_2\text{O}] / 56,168 = 55,01 / 56,168 = 0,978\text{.....}$

$$K_{\text{sp\_eq2}} = \frac{[\text{Na}^+]^2_{\text{aqua}} \cdot [\text{HPO}_4^{2-}]}{57,384^3} = 0,386^3 / 56,168^3 = 3,2456 \cdot 10^{-7}\text{.....};$$

$$\Delta G_{\text{sp\_eq2}} = -R \cdot T \cdot \ln(K_{\text{sp\_eq2}}) = -8,3144 \cdot 298,15 \cdot \ln(3,2456 \cdot 10^{-7}) = 37,037\text{..... kJ}/\text{mol}.$$



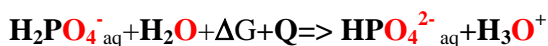
A 50% B+C

$\text{Na}_2\text{HPO}_4(\text{aq})$  crystalline

reactant products



Dihydrogen phosphate deprotonation with water equilibrium



Substance	$\Delta H^\circ_{\text{Hess}}$ , kJ/mol	$\Delta S^\circ_{\text{Hess}}$ , J/mol/K	$\Delta G^\circ_{\text{H}}$ , kJ/mol
<b>OH<sup>-</sup></b>	-230,015	-10,9	-157,2
<b>H<sub>3</sub>O<sup>+</sup></b>	-285,81	-3,854	-3,854
<b>H<sub>2</sub>O</b>	-285,85	69,9565	-237,191
<b>H<sub>2</sub>O</b>	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>
<b>H<sub>2</sub>PO<sub>4</sub><sup>-</sup></b>	-1296,3	90,4	-1130,2
<b>H<sub>2</sub>PO<sub>4</sub><sup>-</sup></b>	-1302,6	92,5	-1137,3
<b>HPO<sub>4</sub><sup>2-</sup></b>	-1292,14	-33,47	-1089,28
<b>HPO<sub>4</sub><sup>2-</sup></b>	<b>-1298,89</b>	<b>-810,792</b>	<b>-1057,143</b>
<b>Na<sup>+</sup><sub>aqua</sub></b>	-240,1	59	-

CRC 2010 1.  $\Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{Reactants}}$   
 2. 1.  $\Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{Reactants}}$   
 3.  $\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$  **endothermic**.....  
 1.  $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{HPO}_4^{2-}} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_2\text{PO}_4^-} - \Delta H^\circ_{\text{H}_2\text{O}} = 10,5 \dots \text{kJ/mol}$   
 $= -1292,14 - 285,81 - (-1302,6 - 285,85) = 10,5 \dots \text{kJ/mol}$   
 2.  $\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}} / T = -10,52 / 298,15 = -35,2 \dots \text{J/(mol K)}$ .  
 Protolysis enthalpy is positive, that exhibit heat consumption, accumulation in products **endothermic** cooling environment.  
 Protolysis entropy is negative, as free energy accumulates, saves in products **HPO<sub>4</sub><sup>2-</sup>aq + H<sub>3</sub>O<sup>+</sup>**.....

$$2. \Delta S_{\text{Hess}} = \Delta S^\circ_{\text{HPO}_4^{2-}} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{H}_2\text{PO}_4^-} - \Delta S^\circ_{\text{H}_2\text{O}} = -33,47 - 3,854 - (92,5 + 69,96) = -199,784 \dots \text{J/mol/K}$$

Protolysis dissociation free energy change  $\Delta G_{\text{Hess}}$  is **endoergic, unfavored**.....:

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 10,5 - 298,15 \cdot (-0,199784) = 70,0 \dots \text{kJ/mol}$$

Entropy sum is negative, as free energy endoergic accumulates, saves in products **HPO<sub>4</sub><sup>2-</sup>aq + H<sub>3</sub>O<sup>+</sup>**.....

$$3. \Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = -199,784 - 35,2 = -234,984 \dots \text{J/(mol K)}$$

Bound free energy in products relative to environment is negative as lost from the surrounding:

$$T \cdot \Delta S_{\text{total}} = -234,984 \text{ J/mol/K} \cdot 298,15 \text{ K} = -70,0 \dots \text{kJ/mol}; \text{ Thermodynamic process unfavored.}$$

Dihydrogen phosphate **H<sub>2</sub>PO<sub>4</sub><sup>-</sup>aq** weak acid  $\text{pK}_a = 7,199$  unfavored classic constant  $\text{K}_a = 10^{-7,199}$ .

$$\text{K}_a = \frac{[\text{HPO}_4^{2-}]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]_{\text{aqua}}} = [\text{H}_2\text{O}] \text{K}_{\text{eq}} = 55,3 \cdot 1,144 \cdot 10^{-9} = 10^{-7,199} \dots = 10^{-\text{pK}_a}; \text{pK}_a = 7,199 \dots;$$

$$\text{Equilibrium constant } \frac{[\text{HPO}_4^{2-}]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = \text{K}_{\text{eq}} = \text{K}_a / [\text{H}_2\text{O}] = 10^{-7,199} / 55,3 = 1,144 \cdot 10^{-9} \dots$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(\text{K}_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(1,144 \cdot 10^{-9}) = 51,0 \dots \text{kJ/mol}$$

Endothermic and endoergic **H<sub>2</sub>PO<sub>4</sub><sup>-</sup>** protolysis Hess free energy change

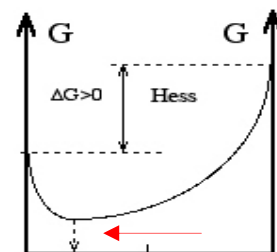
$$\text{positive } \Delta G_{\text{protolysis}} = 70,0 \dots \text{kJ/mol}$$

$$\text{but minimised to } \Delta G_{\text{min}} = \Delta G_{\text{eq}} = 51,0 \dots \text{kJ/mol}$$

$$\text{reached equilibrium mixture } \text{K}_{\text{eq}} = \frac{[\text{HPO}_4^{2-}]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = 1,144 \cdot 10^{-9} \dots$$

Free energy change minimum reaching establish equilibrium mixture.

Weak acid unfavored equilibrium friendly to physiologic pH=7,36



A+B 50% C+D  
**H<sub>2</sub>PO<sub>4</sub><sup>-</sup>aq + H<sub>2</sub>O**  
 reactantss products  
**HPO<sub>4</sub><sup>2-</sup>aq + H<sub>3</sub>O<sup>+</sup>**

Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$ .

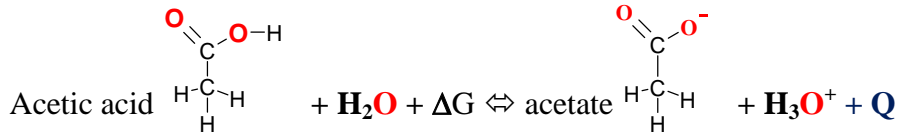
Human organism weak electrolyte solutions are acids: dominate bicarbonate, dihydrogen phosphate and silencing pH=7,36 unaffacting carboxylic acids, amino acids, protonate amines and proteins:

If  $\Delta G$  is positive, **eksponente** has negative power  $e^{-negative}$ , therefore constant  $K_{dis} < 1$  is smaller as one ( $0 < K_{dis} < 1$ ) but newer reach zero 0. Human organism have only weak acids.

**Carboxylic acid- COOH dissociation-protolysis thermodynamic**

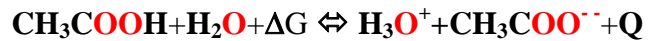
Acetic acid solution deprotonation protolysis:  $CH_3COOH + H_2O + \Delta G \Leftrightarrow H_3O^+ + CH_3COO^- + Q$ ;

Classic constant  $K_a$  over  $[H_2O]$ :  $K_{eq} = \frac{[H^+][CH_3COO^-]}{[H_2O][CH_3COOH]_{nedis}} = K_a / [H_2O] = 1,76 \cdot 10^{-5} / 55,3 = 10^{-6,497} \dots\dots\dots$



Reactants and products standard enthalpies, entropies and free Gibbs energy values:

Viela	$\Delta H_{H,}^{\circ}, kJ/mol$	$\Delta S_{H,}^{\circ}, J/mol/K$	$\Delta G_{Hess,}^{\circ}, kJ/mo$
$H_3O^+$	-285.81	-3.854	-213,275
$H_3CCOO^-$	-486	85.3	85.3
$CH_3COO^-_{aq}$	<b>-486,836</b>	<b>-822,3</b>	<b>-241,663</b>
$H_2O$	-285.85	69.9565	69.9565
$H_2O$	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>
$H_3C-COOH$	-484,09	159,83	-531,743



1.  $\Delta H_{Hess} = \sum \Delta H^{\circ}_{products} - \sum \Delta H^{\circ}_{reactants}$   
 2.  $\Delta S_{Hess} = \sum \Delta S^{\circ}_{pHodukt} - \sum \Delta S^{\circ}_{reactants}$ ; 3.  $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess}$

Protolysis dissociation free energy change

by Hess law  $\Delta G_{Hess}$  is:

$\Delta G_{Hess} = \Delta H_{Hess} - T \Delta S_{Hess}; = -1,87 + 298,15 \cdot 0,1483405 = 42,3577 \dots\dots\dots kJ/mol$  **endoergic**.....

Gibbs free energy change is positive and dissociation in water for weak acid is negligible small.

Little **exothermic** heat evolving dispersed in surrounding of environment:

$\Delta H_{Hess} = \Delta H^{\circ}_{H_3CCOO^-} + \Delta H^{\circ}_{H_3O} - \Delta H^{\circ}_{H_2O} - \Delta H^{\circ}_{H_3CCOOH} =$   
 $= -486 - 285,81 - (-285,85 - 484,09) = -771,81 + 769,94 = -1,87 \dots\dots\dots kJ/mol$   
 2.  $\Delta S_{dispersed} = - \Delta H_{Hess} / T = 1,87 / 298,15 = 6,272011 \dots\dots\dots J/(mol \cdot K)$

Protolysis entropy is negative, that show endoergic free energy accumulation in products.

2.  $\Delta S_{Hess} = \Delta S^{\circ}_{H_3CCOO^-} + \Delta S^{\circ}_{H_3O} - \Delta S^{\circ}_{H_2O} - \Delta S^{\circ}_{H_3CCOOH} =$   
 $= 85,3 - 3,854 - (69,9565 + 159,83) = 81,446 - 229,7865 = -148,3405 \dots\dots\dots J/mol/K$

Total entropy sum negative shows endoergic free energy accumulation in products.:

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

In products bound free energy relative to environment is negative as from surrounding lost:

$T \cdot \Delta S_{total} = -142,0685 J/K/mol \cdot 298,15 K = -42,3577 \dots\dots\dots kJ/mol$ .

At equilibrium reached free energy change minimum for concentration ratio expression of compounds mixture:

$K_{eq} = \frac{[H^+][CH_3COO^-]}{[H_2O][CH_3COOH]_{nedis}} = 1,76 \cdot 10^{-5} / 55,3 = 10^{-6,497} \dots\dots\dots$  Weak acid unfavored equilibrium.

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

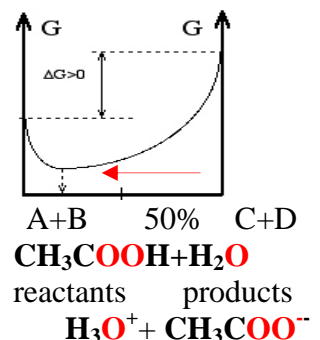
Exothermic and endoergic acetic acid protolysis Hess law free energy change

$\Delta G_{Hess} = \Delta G_{protolysis} = 42,36 \dots\dots\dots kJ/mol$  positive, but minimised at mixture

$\Delta G_{min} = \Delta G_{eq} = 37,085 \dots\dots\dots kJ/mol$  reaching equilibrium :

$K_{eq} = \frac{[H^+][CH_3COO^-]}{[H_2O][CH_3COOH]_{nedis}} = 10^{-6,497}$  . Classic constant includes water concentration

factorial  $K_a = K_{H_3CCOOH} = K_{eq}[H_2O] = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]_{nedis}} = 10^{-6,497} \cdot 55,3 = 10^{-4,76} \dots\dots\dots$ ;



Reaction trends to Prigogine attractor free energy change minimum  $\Delta G_{min}$  .

Free energy change minimum reaching establish equilibrium mixture.

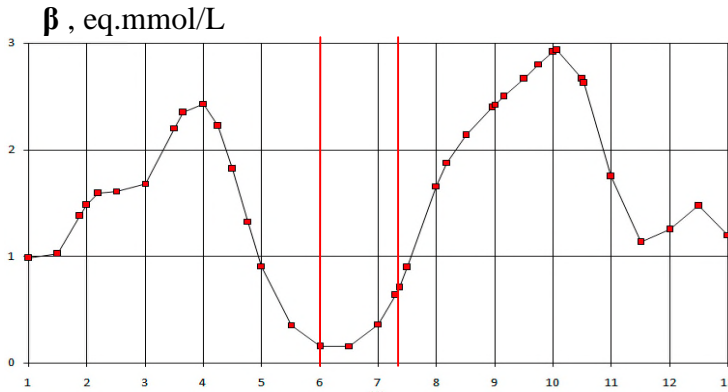
1. Protonate amines the weak acids  $\text{NH}_4^+_{\text{aq}}$  protolysis buffer solutions of proteins and amino acids  
 14<sup>th</sup>, 16<sup>th</sup> page: <http://aris.gusc.lv/BioThermodynamics/CO2O2Thermodynamic15A.pdf>

Weak acid protolysis  $\text{NH}_4^+_{\text{aq}} + \text{H}_2\text{O} + \Delta\text{G} + \text{Q} \rightleftharpoons \text{NH}_3_{\text{aq}} + \text{H}_3\text{O}^+$ ;  $\text{NH}_4^+ = \text{H}^+ + \text{NH}_3_{\text{aq}}$ ;  $\text{pK}_a = 9,25$ ;  
 Classic constants ratio of water constant  $\text{K}_{\text{H}_2\text{O}}$  over apparent  $\text{K}_{\text{NH}_4\text{OH}}$ :

Classic constants ratio:  $\text{K}_{\text{eq}3} = [\text{H}_2\text{O}] * \text{K}_{\text{H}_2\text{O}} / \text{K}_{\text{NH}_4\text{OH}} = [\text{H}_2\text{O}] \frac{3,26 * 10^{-18}}{1,78 * 10^{-5}} = 55,3 * 1,831 * 10^{-13} = 1,013 * 10^{-11}$  .....

Classic value  $\text{pK}_a = -\log([\text{H}_2\text{O}] * \text{K}_{\text{eq}3}) = -\log(55,3 * 1,013 * 10^{-11}) = -\log(5,602 * 10^{-10}) = 9,25$ .....;

Human organism unaffacting the Physiologic  $\text{pH} = 7,36$  weak acids consist of two type functional groups carboxylate  $-\text{COO}^-$  un ammonium  $-\text{NH}_3^+$ :



Carboxylic  $-\text{COOH}$

$\text{pK}_a$  values are on interval from 2 to 5 and protonate amines  $-\text{NH}_3^+$

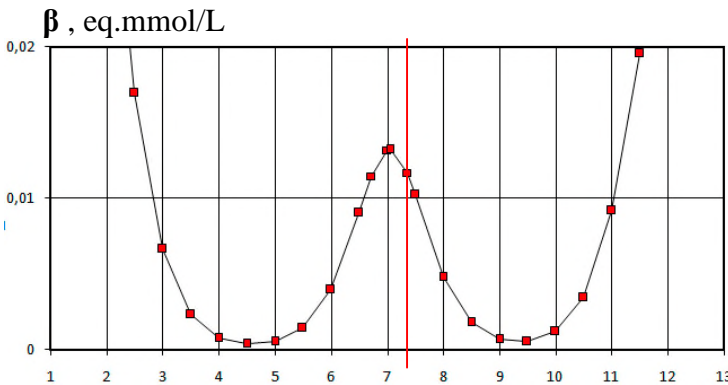
$\text{pK}_a$  values are on interval from 8 to 10 .

Proteins buffer have silence region from  $\text{pH} = 6$  to  $7,36$  .  
 23 thousand protein molecules total buffer solution concentration  $C_{\text{buffer}} = 2,3 \text{ mM}$  . Buffer capacity at physiologic  $\text{pH} = 7,36$  is  $\beta = 0,7 \text{ mM}$   
 $0,09\% = 0,7 / 812,7 * 100\%$

Indispensible inactive silencing interval  $\Delta\text{pH}$  from 6 to  $7,36$

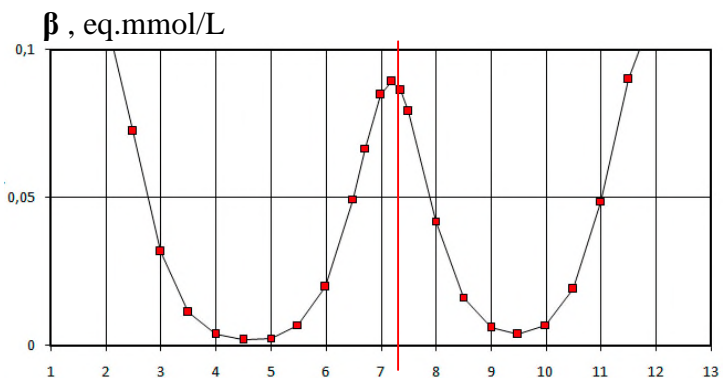
providing attractor  $\text{pH} = 7,36$  with two dominate buffer systems Bicarbonate and Phosphate :

2. Bicarbonate  $\text{CO}_2_{\text{aqua}} + 2 \text{H}_2\text{O} + \Delta\text{G} + \text{Q} \xrightleftharpoons{\text{CA}} \text{H}_3\text{O}^+ + \text{HCO}_3^-$ ;  $\text{pK}_a = -\log(2,906 * 10^{-11} * 55,3^2) = 7,0512$ .....;



Total bicarbonate buffer system concentration  $[\text{CO}_2_{\text{aqua}}] + [\text{HCO}_3^-]$  in blood plasma is  $C_{\text{buffer}} = 0,023 \text{ M}$  . Buffer capacity at physiologic  $\text{pH} = 7,36$  is  $\beta = 12 \text{ mM}$   
 $1,4\% = 12 / 812,7 * 100\%$

3. Dihydrogenphosphate  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} + \Delta\text{G} + \text{Q} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$   $\text{pK}_a = 7,199$  .



Total phosphate buffer systems concentration  $[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$  in muscle cells cytosole is  $C_{\text{buffer}} = 0,155 \text{ M}$  . Buffer capacity at physiologic  $\text{pH} = 7,36$  is  $\beta = 800 \text{ mM}$   
 $98,44\% = 800 / 812,7 * 100\%$

Life solutions form favored and unfavored reactions with water reaching equilibria as product,

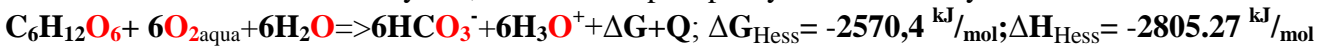
equilibrium=solubility constant  $\text{K}_{\text{eq}} = \text{K}_{\text{sp}}$  , free energy change minimum  $\Delta\text{G}_{\text{min}}$  at equilibrium state.

Four types synthesis and decomposition reactions occur in environment of life solutions.

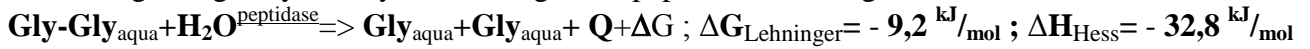
## Synthesis and Decomposition reactions four types

### 1. EXOTHERMIC, EXOERGIC DECOMPOSITION REACTION of hydrolysis and bio oxidation

Oxidoreductases E.1 classes enzymes, as oxidative phosphorylation summary:



E.3 class degrading enzymes Hydrolases-digestive peptidases : exoergic exothermic



This type of reaction can be written in a general way as: exoergic exothermic::



one can see, that the first component of it ( $\Delta\text{H}$ ) is negative.  $\Delta\text{S}$  itself is positive, but as there is a minus sign before it, the second component of it ( $-\text{T} \cdot \Delta\text{S}$ ) is also negative. This means, that  $\Delta\text{G}$  is always negative for this type of reactions.. **Conclusion:** an exothermic decomposition reaction is spontaneous at all conditions.

### 2. EXOTHERMIC REACTIONS OF SYNTHESIS

An **EXOTHERMIC REACTION OF SYNTHESIS** in a general way can be written as:



the first component  $\Delta\text{H}$  of the equation is negative, but the second one - positive ( $\Delta\text{S}$  is itself negative, but there is a minus sign before it). As one of the components is positive, but the other negative, the result  $\Delta\text{G}$  can be negative, if the negative component  $\Delta\text{H}$  by its absolute value is greater, than the positive component ( $-\text{T}\Delta\text{S}$ ):

$$|\Delta\text{H}| > |\text{T} \cdot \Delta\text{S}|$$

This is possible, if the temperature is low enough human body temperature 310.15 K

**Conclusion:** A synthesis reaction, that is exothermic, is spontaneous at low enough temperatures.

### 3. ENDOTHERMIC , EXOERGIC REACTION OF DECOMPOSITION

An example of an endothermic reaction of decomposition in a general form can be written as:



Thus, the first component ( $\Delta\text{H}$ ) in the equation is positive, but the second one ( $-\text{T} \cdot \Delta\text{S}$ ) - negative as entropy change itself is a positive value, but the minus sign in the equation turns the second component of equation negative.

In such a way, the change of Gibbs's Energy  $\Delta\text{G}$  can be negative (and the reaction can be spontaneous), if the negative component is greater, than the positive one:  $|\text{T} \cdot \Delta\text{S}| > |\Delta\text{H}|$

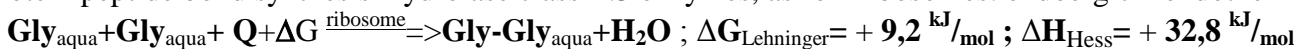
An endothermic reaction of decomposition occurs spontaneously at high enough temperatures.

### 4. ENDOTHERMIC, ENDOERGIC REACTION OF SYNTHESIS.

Oxidoreductase class E.1 enzymes, as for photosynthesis: endoergic endothermic:



Protein peptide bond synthesis hydrolase class E.3 enzymes, as for Ribosomes: endoergic endothermic:



This kind of reactions can be generally expressed as:  $\text{A} + \text{B} \Rightarrow \text{AB}; \quad \Delta\text{S} < 0 \quad \text{and} \quad \Delta\text{H} > 0$ .

Both components of  $\Delta\text{G}$  are positive and therefore  $\Delta\text{G}$  is positive at any temperature. It means, that this type of reaction can never be spontaneous, *an endothermic reaction of synthesis is thermodynamically forbidden.*

We can easily notice, that cases 1 and 4 and cases 2 and 3 are reverse reactions to each other.

Two more **conclusions** can be done:

1) *If the direct reaction is always spontaneous, the reverse one is forbidden.(cases 1 and 4).*

2) *If the direct reaction is spontaneous at high temperatures, the reverse one must be carried out at low temperatures.*

## Biochemical Thermodynamics

**Thermodynamics** is the quantitative study of the energy **G** transductions in living organisms the pathways and functions of the **chemical processes** by Ilya Prigogine defined dissipative structure consisting complex systems. Irreversible processes working, with certain attractors driven Brownian molecular engines.

Enzymes and its complexes .



## Attractors aspiration to equilibrium drive enzymes complexes reactions

irreversibility through Pathways **homeostasis** in life solutions of cellular environments.

Five type enzymes reactions complexes sustaining through life **homeostasis**  
irreversibly trends to Prigogine attractors free energy change minimums  $\Delta G_{\min}$ .

Five type complexes reaction order versus chaos of non enzymatic reactions:

1. Gradual-sequential reactions, versus unorganized chaos;
2. ENZYMES **specificity** 100% efficiency of product **singularity**; PARALLEL reactions chaos;
3. Joint-tandem reactions, versus inactive, non reactive, silencing reactants stiff;
4. Competitive-regulatory metabolites complexes versus chaos and contamination;
5. Enzyme radical reactivity for life resources, versus destructive contamination.

### 5 complex Enzyme reactions

Versus non Enzymatic reactions

chaos and contamination

Enzyme governed complex reactions drive the LIFE in 5 ways

7<sup>th</sup> page: <http://aris.gusc.lv/BioThermodynamics/Kinetics.pdf>

#### 1. GRADUAL-CONSECUTIVE organized

7<sup>th</sup> page: <http://aris.gusc.lv/BioThermodynamics/Kinetics.pdf>  
favored reaction sequence of **ENZYME** complexes for  
Glycolysis, Krebs cycle; Polycondensation: Replication,  
Polymerisation, Proteins Translation Synthesis

1. Chaotic

#### 2. ENZYMES **specificity** 100% efficiency of product **singularity**

2. **PARALLEL** reaction preseeded in chemistry as side products

#### 3. **JOINT-TANDEM** SYNTHESIS

Ribosomes for polypeptides, proteins  
Photosynthesis glucose and oxygen

Thermodynamic forbidden impossible reaction  
unfavored is positive free energy change  $\Delta G = \Delta H - \Delta S \cdot T > 0$

1<sup>st</sup> to 5<sup>th</sup> page: <http://aris.gusc.lv/BioThermodynamics/74LidzsvarsDabaEngl.pdf>

#### 4. **COMPETITIVE** regulation as inhibition and allostery

sensitive to concentration  $O_{2\text{aqua}}$ ,  $HC O_3^-$ ,  $H^+$  (Le Chatelier principle)

His63,58 as for hemoglobin, His64 as for myoglobin as regulated back response

prevent (hypo amount) deficiency and (hyper amount) overproduction

so stabilises Physiologic pH=7.36, venouse  $[O_{2\text{aqua}}]=1.8 \cdot 10^{-5}$  M and arterial  $[O_{2\text{aqua}}]=6 \cdot 10^{-5}$  M.

Photosynthesis global stabilises oxygene concentration  $[O_{2\text{AIR}}]=20,95\%$  in Earth Atmosphere.

4. Chaotic

#### 5. Enzyme radical driven reactivity the process for maintenance of homeostasis producing resources

5. Contamination destructive chemistry with the chaotic radical chain reactions in multiple parallel products

# Homeostasis instruments