

Medical Chemistry show functional active molecules formation conditions as attractors.

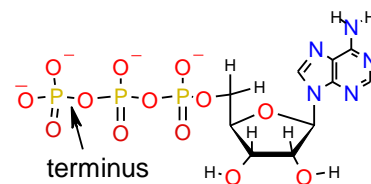
In cell membrane compartments **solutions** are irreversible products. Dissipative structure consisting molecules are functional activate in complex irreversible reactions enzymes clusters. Which drive as the Brownian molecular engines the evolution, surviving and homeostasis, while high rate protolysis attractors  $\text{pH}=7.36\pm 0,01$ , AIR oxygen  $[\text{O}_2]=20.95\%$ , CA Carbonic Anhydrase,  $\text{H}_2\text{O}$  stay at equilibrium. Nobel Prize in Chemistry 1977<sup>th</sup>.

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  $\text{O}_2$  gas, carbon dioxide  $\text{CO}_2$  gas, hydrogen chloride  $\text{HCl}$  , ammonia, amines  $\text{NH}_3$ . In water dissolute crystalline salt sodium chloride  $\text{NaCl}_s$  , sodium acetate  $\text{CH}_3\text{COONa}_s$  , ammonium chloride  $\text{NH}_4\text{Cl}_s$  , sodium dihydrogen phosphate  $\text{NaH}_2\text{PO}_4$  , sodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4$  ,

In water dissolute carboxylic acids, amino acids and amines as weak acids  $\text{pK}_a$  interval  $\text{pH}=2$  to  $10$ .

Weak acids react with water. Ammonium cations  $\text{NH}_4^+_{aq}$  consist in protonate state at  $\text{pH}=7,36$  Biochemistry attractor, which deprotonate all carbonic acids and phosphates to carboxylates  $-\text{COO}^-$  , hydrogen  $\text{HPO}_4^{2-}$  phosphates and deprotonate poly phosphate terminus  $-\text{PO}_4^{2-}$  like  $\text{ATP}^+$  ions .



Protolytic equilibria stay at biochemistry attractors  $C_{osm}=0,305$  M,  $I=0,25$  M and  $\text{pH}=7,36$ : Acids are carboxylic, amino acids, protonate amines , proteins , dihydrogen phosphates, terminus of poly phosphates.

Classic example is acetic acid  $\text{CH}_3\text{COOH}$  and ammonium ion  $\text{NH}_4^+_{aq}$  protolytic reaction with water and Ostwald dilution law dissociation degree  $\alpha = \sqrt{\frac{K_a}{C}}$  for weak acetic acid :  $[\text{H}_3\text{O}^+] = \sqrt{K_a \cdot C} = 10^{-\text{pH}}$  Molarity

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

$\text{O}_{2\text{aqua}}$  solution osmosis through aquaporin channels forms blood plasma  $\text{O}_{2\text{aqua-blood}}$  solution .

Living organisms dissolute oxygen in osmosis through E7 class transport enzymes membrane aquaporins against concentration gradient forms normal concentration  $\text{O}_{2\text{aqua-Blood}}$  isooxia.

Poor 100% oxygen gas mol fraction is  $[\text{O}_{2\text{gas}}] = 1$  . Atmosphere oxygen 20,95% mol fraction is 0,2095. Air 20,95% solubility  $[\text{O}_{2\text{aqua}}]=K_{O_2} \cdot [\text{O}_{2\text{air}}]=1,22 \cdot 10^{-3} \cdot 0,2095=2,556 \cdot 10^{-4}$  M. Solubility in plasma  $[\text{O}_{2\text{aqua}}]=9,768 \cdot 10^{-5}$  M if osmolar and ionic strength concentrations are  $C_{osm}=0,305$  M,  $I=0,25$  M. Zero osmolar and ionic strength concentrations  $C_{osm}=0$  and  $I=0$  M as distilled water solubility is  $[\text{O}_{2\text{aq}}]=2,556 \cdot 10^{-4}$  M . At osmolar, ionic strength, AIR oxygen concentration  $C_{osm}=0,305$  M,  $I=0,25$  M, 20,95% the Physiologic interface to AIR is  $K_{O_2\text{Blood}}=[\text{O}_{2\text{aqua}}]/[\text{O}_{2\text{air}}]=9,768 \cdot 10^{-5}/0,2095=4,663 \cdot 10^{-4}=10^{-3,3314}=10^{\text{pK}_{O_2\text{Blood}}}$ . Homeostasis arterial  $[\text{O}_{2\text{aqua}}]=6 \cdot 10^{-5}$  M and venous concentration is  $[\text{O}_{2\text{aqua}}]=0,426 \cdot 10^{-5}$  M. [Lehninger](#) :

Hyperoxia over isoxia  $\text{O}_2$  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 induces hypoxia induced factors cell proteins HIF, which work on nuclear receptors switching processes with decreased oxygen concentration - deficiency. Nobel Prize in Medicine 2019 .

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

Solubility at 25° C 298,15 K  $[O_{2,aqua}] = K_{O_2} = 1,22 \cdot 10^{-3} M$ , if 100% oxygen in gas mol fraction is  $[O_{2,air}] = 1$ .

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

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

Mol fraction of water solution is ratio :  $[O_{2,aqua}]/[H_2O] = K_{O_2}/[H_2O]$ .

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

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

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

Substance	$\Delta H^\circ_{Hess}, kJ/mol$	$\Delta S^\circ_{Hess}, J/mol/K$	$\Delta G^\circ_{Hess}, kJ/mol$
$O_{2,aqua}$	<b>-11,70</b>	<b>-94,2</b>	<b>16,40</b>
$O_{2,aqua}$	-11,715	110,876	16,4
$O_2 \uparrow_{gas}$	0	205,152	0
$H_3O^+$	-285,81	-3,854	-213,275
$CO_2_{gas}$	<b>-393,5</b>	<b>2,9</b>	<b>-394,36</b>
			$G_{gr} = -91,26$
			$G_{O_2_{gas}} = 303,1$
$H_2_{gas}$	<b>-0,82</b>	<b>-283,82</b>	<b>85,64</b>
$H_2O$	-285,85	69,9565	-237,191
$H_2O$	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>

$O_2 \uparrow_{air} + H_2O + \Delta G_{Akaporini} \rightarrow O_{2,aqua} + H_2O + Q$   
**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.  $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess}$   
 $\Delta G_{Hess} = \Delta G^\circ_{H_2O} + \Delta G^\circ_{O_{2,aqua} - Blood} - \Delta G^\circ_{H_2O} - \Delta G^\circ_{O_2_{gas} - AIR} = 16,4$  kJ/mol;  
 CRC 2010;  $= 16,4 - 151,549 - (0 + (-151,549)) = 16,4$  kJ/mol **exoergic**  
 $\Delta G_{Hess\_CO_2_{gas}} = G^\circ_{CO_2_{gas}} - (G_{gr} + G_{O_2}) = 0 - (91,26 + 303,1) = -394,36$   
 $G_{gr} = -\Delta G_{Hess\_CO_2_{gas}} - G_{O_2_{gas}} = 394,36 - 303,1 = 91,26$  kJ/mol.  
 $G_{O_2_{gas}} = (-G^\circ_{H_2O} - G^\circ_{H_2_{gas}}) \cdot 2 = (237,19 - 85,64) \cdot 2 = 303,1$  kJ/mol;  
 $G^\circ_{H_2_{gas}} = 85,64$  kJ/mol; Alberty R.A. Biochem. Thermodynamic's 463, 2006  
 1.  $\Delta H_{Hess} = \Delta H^\circ_{H_2O} + \Delta H^\circ_{O_{2,aqua} - Blood} - \Delta H^\circ_{H_2O} - \Delta H^\circ_{O_2_{gas} - AIR} = -11,75$  kJ/mol;  
 $= -11,7 - 286,65 - (0 + (-286,65)) = -11,7$ ..... kJ/mol **exothermic**.....

$\Delta S_{dispersed} = -\Delta H_{Hess}/T = 11,7/298,15 = 39,24$  J/mol/K ;

$\Delta S_{Hess} = \Delta S^\circ_{H_2O} + \Delta S^\circ_{O_{2,aqua} - Blood} - \Delta S^\circ_{H_2O} - \Delta S^\circ_{O_2_{gas} - AIR} = -94,2 - 453,188 - (205,152 - 453,188) = -299,352$  J/mol/K;

$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = -299,352 + 39,24 = -260,112$  J/mol/K ;

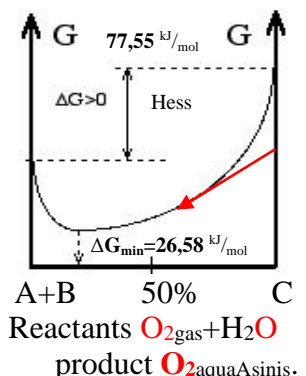
3.  $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess} = -11,7 - 298,15 \cdot (-0,299352) = 77,55$  kJ/mol **endoergic**.....

$T \cdot \Delta S_{total} = -0,260112$  kJ/K/mol  $\cdot 298,15K = -77,55$  kJ/mol; bound  $T \Delta S_{n} \leftarrow$  accumulate energy.unfavored ;

Hess law calculation is exothermic and endoergic

oxygen solubility havng free energy change positive

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



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

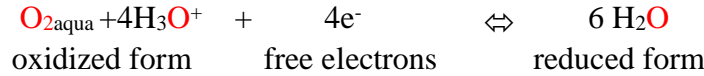
Le Chatelier principle is Prigogine attractor for Free energy change minimum  $\Delta G_{min}$  reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium. 53<sup>th</sup> page:

**Nernst's potential  $O_{2,aqua}/H_2O$**  red-ox system mechanism of acidosis and oxidative stress hazard of high oxidizing agent power potential E in Volts and free energy in kilojoules per mol.

Note: Oxidative stress causes **non enzymatic** oxidation in multiple radical chain and reactions of parallel product formations to contaminate and destroy the organism! Destructive hazard for life!

Water medium (blood plasma) oxygen is strong oxidant according thermodynamic standard potential **1,383 V**:



Arterial [ $\text{O}_{2\text{aqua}}$ ]= $6 \cdot 10^{-5}$  M , pH=7.36 concentration [ $\text{H}_3\text{O}^+$ ]= $10^{-7.36}$  M and water [ $\text{H}_2\text{O}$ ]=55.346 M.

$$E_{\text{O}_2} = E^\circ + 0.0591/4 \cdot \log([\text{O}_{2\text{aqua}}] \cdot [\text{H}_3\text{O}^+]^4 / [\text{H}_2\text{O}]^6) = 1.383 + 0.0591/4 \cdot \log(6 \cdot 10^{-5} \cdot 10^{(-7.36 \cdot 4)} / 55.346^6) = 0.731 \text{ Volts} .$$

Oxidative stress risk decrease minimize potential  $\Delta E_{\text{arterial}} = E^\circ - E_o = 1.383 - 0.731 = -0.652$  Volts; 5<sup>th</sup> [page](#) .

Free energy content for oxygen decreases  $\Delta G_{\text{arterial}} = \Delta E_{\text{H}_2\text{O}} \cdot F \cdot n = -0.652 \cdot 96485 \cdot 4 / 1000 = -251.6$  kJ/mol.

1) Water [ $\text{H}_2\text{O}$ ] =  $996.23/18 = 55.346$  M decreases potential from **1.383 V** to classic standard **1.228 V**

about **-0.155 V** =  $\Delta E_{\text{H}_2\text{O}}$ ;  $E_o = E^\circ + 0.0591/4 \cdot \log(1 / [\text{H}_2\text{O}]^6) = 1.383 + 0.01478 \cdot \log(1 / 55.346^6) = 1.228$  V ;

Oxidative stress risk decrease about  $\Delta E_{\text{H}_2\text{O}} = E^\circ - E_o = 1.228 - 1.383 = -0.155$  V and minimized free

energy content for oxygen about  $\Delta G_{\text{min}} = \Delta E_{\text{H}_2\text{O}} \cdot F \cdot n = -0.155 \cdot 96485 \cdot 4 / 1000 = -59.82$  kJ/mol;

Total oxidative stress risk decrease  $\Delta G_{\text{min}} = \Delta E_{\text{O}_{2\text{aqua}} \text{ pH}} + \Delta G_{\text{H}_2\text{O}} = -192.22 - 59.82 = -251.6$  kJ/mol;

2) Acid concentration [ $\text{H}_3\text{O}^+$ ] increases 10 times the potential increases about  $\Delta E_{\text{H}_3\text{O}^+} = 0.05912$  V .

$$\Delta E_{\text{H}_3\text{O}^+} = 0.01478 \cdot \lg([\text{H}^+]^4) = 0.01478 \cdot \lg(10^4) = 0.05912 \text{ V}; \text{ Free energy content for}$$

oxygen increases about  $\Delta G_{\text{max}} = \Delta E_{\text{H}_3\text{O}^+} \cdot F \cdot n = 0.05912 \cdot 96485 \cdot 4 / 1000 = 22.817$  kJ/mol;

3) Air 20.95% instead pure 100% oxygen [ $\text{O}_{2\text{aqua}}$ ] concentration is 5 times lower with decreased potential:

$$\Delta E_{\text{O}_{2100\%}} = 0.01478 \cdot \lg(100\% [\text{O}_{2\text{aqua}}]) = 0.01478 \cdot \lg(1/5) = -0.0103 \text{ V} . \text{ Free energy content for}$$

20.95% oxygen decreases about  $\Delta G_{\text{max}} = \Delta E_{\text{H}_3\text{O}^+} \cdot F \cdot n = -0.01033 \cdot 96485 \cdot 4 / 1000 = -3.987$  kJ/mol; 6<sup>th</sup> [page](#):

NASA Apollo Moon project closes 1972 because of 100% [ $\text{O}_{2\text{aqua}}$ ] oxidative stress and technical hazards risk.

Which concentration water [ $\text{H}_2\text{O}$ ], oxidant [Ox], reducer [Red], acid [ $\text{H}_3\text{O}^+$ ] changes decrease free energy content or increase free energy content for oxidant? How potential  $E_o$  values change free energy content in oxidants and in reductants ! When free energy content increases and when decreases content?

Zero osmolar  $C_{\text{osm}} = 0$  M and ionic force  $I = 0$  M in distilled water from air 20.95% solubility is:

$$[\text{O}_{2\text{water}}] = K_{\text{eq}} \cdot [\text{O}_{2\text{air}}] \cdot [\text{H}_2\text{O}] = 2.205 \cdot 10^{-5} \cdot 0.2095 \cdot 55.3 = 2.5567 \cdot 10^{-4} \text{ M} .$$

[ELSEVIER](#), Rotating Electrode Method and Oxygen reduction Electrocatalysts, 2014, p.1-31,

1. WeiXinga, MinYinb, QingLv, YangHub, ChangpengLiub, JiuJunZhangc. Pure 1atm mol fraction [ $\text{O}_{2\text{gas}}$ ]=1.

Osmolar  $C_{\text{osm}} = 0.305$  M, ionic force  $I = 0.25$  M, air oxygen 20.95% conditions dissolve [ $\text{O}_{2\text{aqua}}$ ]= $9.768 \cdot 10^{-5}$  M.

Therefore physiologic equilibrium constant is  $K_{\text{O}_{2\text{blood}}} = [\text{O}_{2\text{aqua}}] / [\text{O}_{2\text{air}}] = 9.768 \cdot 10^{-5} / 0.2095 = 4.663 \cdot 10^{-4} = 10^{-3.3314}$ .

[Arterial](#) [ $\text{O}_{2\text{aqua}}$ ]= $6 \cdot 10^{-5}$  M and venous [ $\text{O}_{2\text{aqua}}$ ]= $0.426 \cdot 10^{-5}$  M concentration determines  $\text{p}K_{\text{O}_{2\text{blood}}} = 3.3314$

by osmosis oxygen molecules crossing through aquaporins membranes against gradient.

If metabolism products biochemical zero values are  $G_{\text{H}_2\text{O}} = 0$  kJ/mol for water and  $G_{\text{CO}_2\text{gas}} = 0$  kJ/mol .

[Alberty](#) [8] free energy for hydrogen gas  $G^\circ_{\text{H}_2\text{gas}} = 85.64$  kJ/mol lets [appreciate](#) oxygen  $G_{\text{O}_{2\text{aqua}}} = 329.68$  kJ/mol , as in water dissolve oxygen total free energy content in sum is:  $G_{\text{O}_{2\text{aqua}}} = G_{\text{O}_{2\text{gas}}} + G_{\text{O}_{2\text{sp}}} = 303.1 + 26.58 = 329.68$  kJ/mol and graphite free energy content is  $G_{\text{gr}} = -\Delta G_{\text{Hess\_CO}_2\text{gas}} - G_{\text{O}_{2\text{gas}}} = 394.36 - 303.1 = 91.26$  kJ/mol .

Free energy  $G_{\text{O}_{2\text{Biochem\_arterial}}} = G_{\text{O}_{2\text{gas}}} + G_{\text{O}_{2\text{sp}}} + \Delta G_{\text{arterial}} = 303.1 + 26.58 - 251.6 = 78.08$  kJ/mol high rate protolysis decreases and oxygen becomes fire safe biochemical oxidant, forming [arterial concentration](#) [ $\text{O}_{2\text{aqua}}$ ]= $6 \cdot 10^{-5}$  M as safe Bioenergetic sustaining isooxia norma. [3]

Air 0.04% mol fraction [ $\text{CO}_2 \uparrow_{\text{air}}$ ]=0.0004 as 400 ppm parts per million of air dissolve:

$[\text{CO}_2 \text{aqua}] = K_{\text{eq}} * [\text{CO}_2 \uparrow_{\text{air}}] = 1.878 * 0.0004 = 0.0007537 \text{ M}$  concentration. 4<sup>th</sup>, 45<sup>th</sup>, 46<sup>th</sup> pages:

$\text{CO}_2$  solubility product  $K_{\text{sp}} = [\text{CO}_2 \text{aqua}] / [\text{CO}_2 \text{gas}] / [\text{H}_2\text{O}] = 1/29.44$  and reaction with  $\text{OH}^-$  ions.

$\text{CO}_2 \uparrow_{\text{gas}}$  no reaction with  $\text{H}_2\text{O}$  solubility constant  $K_{\text{sp}} = 0.03397$ . 298.15 K.  $[\text{HCO}_3^-] + \text{CA} + [\text{CO}_2 \text{aqua}] = 0.023 \text{ M}$

$\leftarrow$  Reverse for photosynthesis direct reaction for oxidation processes  $\Rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \Rightarrow \text{CO}_2 \text{aqua} + 2\text{H}_2\text{O} + \text{Q} + \Delta\text{G}$

Substance	$\Delta H^\circ_{\text{Hess}}$ , kJ/mol	$\Delta S^\circ_{\text{Hess}}$ , J/mol/K	$\Delta G^\circ_{\text{Hess}}$ , kJ/mol
$\text{H}_3\text{O}^+$	-285.81	-3.854	-213.274599
$-\text{OH}^-$	-230.015	-10.9	-157.2
$\text{HCO}_3^-$	-689.93	98.324	-586.93988
$\text{HCO}_3^-$	<b>-692.4948</b>	<b>-494.768</b>	<b>-544.9688</b>
$\text{H}_2\text{O}$	-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
$\text{CO}_2 \uparrow_{\text{gas}}$	-393.509	213.74	-394.359

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}};$$

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

$$\Delta G_{\text{Hess}} = 2\Delta G^\circ_{\text{H}_2\text{O}} + \Delta G^\circ_{\text{CO}_2} - \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{HCO}_3^-} = -102 \text{ kJ/mol}$$

$$= 2 * -237.191 - 385.98 - (-213.2746 - 544.9688) = -102 \text{ kJ/mol};$$

$$\Delta H_{\text{H}} = 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{HCO}_3^-} = -7.1928 \text{ kJ/mol}$$

$$= 2 * -285.85 - 413.7976 - (-285.81 - 692.4948) = -7.1928 \text{ kJ/mol}$$

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}} / T = 7.1928 / 298.15 = 24.125 \text{ J/mol/K};$$

$$\Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = 756.1054 + 24.125 = 780.23 \text{ J/mol/K};$$

$$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -7.193 - 298.15 * 0.7561 = -232.6 \text{ kJ/mol};$$

$\Delta S_{\text{Hess}} = 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{CO}_2} - \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{HCO}_3^-} = 2 * 69.9565 + 117.5704 - (-3.854 - 494.768) = 756.1054 \dots \text{ J/mol/K}$  **exoergic...**

$T \cdot \Delta S_{\text{total}} = 0.78023 * 298.15 \text{ K} = 232.63 \text{ kJ/mol}$ ; bound  $T \Delta S_{\text{total}}$  accumulate energy endoergic, non spontaneous

CAII; RBCs, kidney, osteoclasts, eye, GI tract,

lungs except alveolar epithelia, brain, and testis; Cytosol; Glaucoma, epilepsy, edema, altitude sickness;

$k_{\text{cat}} = 1.4 \times 10^6 \text{ s}^{-1}$ ;  $k_1 \text{CO}_2 \text{aqua} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ; **Biomed Res Int. 2015:453543. Review Article 3KS3.PDB,**  
 $v_1 = k_1 \text{CO}_2 \text{aqua} [\text{CO}_2 \text{aqua}] = 1.5 * 10^8 * 0.0007537 = 1.14 * 10^6 \text{ s}^{-1}$ ; as  $v_1 = k_{\text{cat}} / K_M * [E]_i [S]_i$ ;  $[E]_i = 1 \text{ M}$ ;  $[S]_i = [\text{CO}_2 \text{aqua}]$ ;

CAII:  $\text{CO}_2 \text{aqua} + 2\text{H}_2\text{O} + \Delta\text{G} + \text{Q} = v_1 \xrightarrow{\text{CA}} \text{H}_3\text{O}^+ + \text{HCO}_3^-$ ;  $\text{pH} = 7.36$ ,  $\text{pOH} = 6.64$ ;  $\text{CO}_2 \text{aqua} \xleftarrow{\text{CA}} \text{H}_3\text{O}^+ + \text{HCO}_3^-$ ;

First approach:  $k_2 = k_1 \text{CO}_2 \text{aqua} [\text{CO}_2 \text{aqua}] / [\text{H}_3\text{O}^+] [\text{HCO}_3^-] = 1.5 * 10^8 * 0.000754 / 10^{-7.36} / 0.0154 = 1.682 * 10^{14} = 10^{14.23} \text{ M}^{-2} \text{ s}^{-1}$ ;

$k_2 / k_1 \text{CO}_2 \text{aqua} = 10^{14.23} / 1.5 / 10^8 = 1132162$  and  $k_1 \text{CO}_2 \text{aqua} / k_2 = 1.5 * 10^8 / 1.682 * 10^{14} = 2.902 * 10^{-11}$

$$K_a = K_{\text{eq}} * [\text{H}_2\text{O}]^2 = 2.902 * 10^{(-11)} * (55.3457339)^2 = 8.892 * 10^{(-8)} = 10^{(-7.0512)} = \frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}}$$

Solution for neutralization velocity constant  $k_2 = k_1 \text{CO}_2 \text{aqua} / K_{\text{eq}} = 1.5 * 10^8 / 2.902 / 10^{(-11)} = 5.16885 * 10^{18} \text{ M}^{-2} \text{ s}^{-1}$ ;

Neutralization  $\text{H}_3\text{O}^+ + \text{HCO}_3^- \Rightarrow \text{CO}_2 \text{aqua} + 2\text{H}_2\text{O}$  velocity according bicarbonate concentration in ocean

$\text{pOH}_{\text{ocean}} = 5.9$ ;  $\text{pH}_{\text{ocean}} = 8.1$ ;  $[\text{HCO}_3^-] = 0.003 \text{ M}$ ; Haack Weltmeer Atlas 1969:

$$v_2 = k_2 \cdot [\text{H}_3\text{O}^+] [\text{HCO}_3^-] = 5.16885 * 10^{18} * 10^{(-8.1)} * 0.003 = 123172905 \text{ s}^{-1}$$

Extra Mitochondrial  $\text{pH} = 5$   $v_2 = k_2 \cdot [\text{H}_3\text{O}^+] [\text{HCO}_3^-] = 5.16885 * 10^{18} * 10^{(-5)} * 0.0154 = 796002900000 \text{ s}^{-1}$ ;

Velocity  $\text{H}_3\text{O}^+ + \text{HCO}_3^- \Rightarrow \text{CO}_2 \text{aqua} + 2\text{H}_2\text{O}$ ;  $k_2 = k_1 \text{CO}_2 \text{aqua} [\text{CO}_2 \text{aqua}] / [\text{H}_3\text{O}^+] [\text{HCO}_3^-] = 5.16885 * 10^{18} \text{ M}^{-2} \text{ s}^{-1}$

neutralization constant is greater the slow hydroxide anions reaction  $k_1 \text{OH}^- = 1.5 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$  times  $10^{16.54}$ :

$k_2 / k_1 \text{OH}^- = 5.16885 * 10^{18} / 1.5 / 10^2 = 10^{16.54}$   $\text{CO}_2 \text{aqua} + \text{OH}^- + \Delta\text{G} + \text{Q} \Rightarrow \text{HCO}_3^-$  and velocity according

concentrations  $v_1 \text{OH}^- = k_1 \text{OH}^- [\text{CO}_2 \text{aqua}] [\text{OH}^-] = 1.5 * 10^2 * 0.0007537 * 10^{(-6.64)} = 2.59 * 10^{-8} \text{ s}^{-1}$ ;

Velocity with hydroxide  $k_1 \text{OH}^- / k_1 \text{CO}_2 \text{aqua} = 1.5 * 10^2 / 1.5 / 10^8 = 10^{-6}$  million times slower as CA.

$\text{OH}^-$  more unfavored due to CA absence  $K_{\text{OH}} = k_1 \text{OH}^- / k_2 = 1.5 * 10^2 / 5.16885 / 10^{18} = 2.90 * 10^{(-17)} = \frac{[\text{HCO}_3^-]}{[\text{CO}_2]_{\text{aqua}} \cdot [\text{OH}^-]}$

$\Delta G_{\text{OH}} = -R \cdot T \cdot \ln(K_{\text{OH}}) = -8.3144 * 298.15 * \ln(2.902 * 10^{(-17)}) / 1000 = 94.4 \text{ kJ/mol}$ ;

Neutralization is faster 34459000000 times over CA driven velocity constant  $k_1 \text{CO}_2 \text{aqua} = 1.5 * 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ;

$k_2 / k_1 \text{CO}_2 \text{aqua} = 5.16885 * 10^{18} / 1.5 / 10^8 = 34459000000$  times.

Exothermic and exoergic neutralization  $\text{H}_3\text{O}^+ + \text{HCO}_3^- \rightleftharpoons \text{CO}_2 \text{aqua} + 2\text{H}_2\text{O}$  Hess free

energy  $\Delta G_{\text{neutralization}}$  negative  $-102 \text{ kJ/mol}$ , but minimized  $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -60 \text{ kJ/mol}$

reaching equilibrium mixture  $K_{\text{eq}} = 1 / 2.902 / 10^{(-11)} = 34459000000$  at presence of CA

Carbonic Anhydrase. Le Chatelier principle is Prigogine attractor free energy change

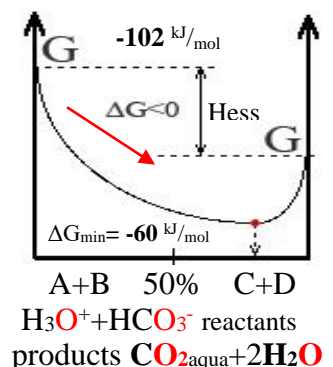
minimum reaching  $\Delta G_{\text{min}}$  at equilibrium mixture. Free energy minimum reaching

establishes equilibrium. Reaction with hydroxide anion is slow and never reach

equilibrium: Carbonic Anhydrase is the key enzyme for bicarbonate buffer system on

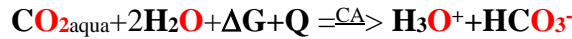
planet Earth.

4<sup>th</sup> page:





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.

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

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

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

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

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

$$3. \Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_3\text{O}^+} + \Delta G^\circ_{\text{HCO}_3^-} - 2\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{CO}_2} = -213.2746 - 544.9688 - (2 \cdot -237.191 - 385.98) = 102 \dots \text{kJ/mol};$$

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

$$\text{Ratio in constant: } \text{K}_{\text{eq}} = \frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}} \cdot [\text{H}_2\text{O}]^2} = \text{K}_{\text{HCO}_3} / [\text{H}_2\text{O}]^2 = 10^{-7.0512} / 55.3^2 = 2.906 \cdot 10^{-11} \dots$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(\text{K}_{\text{eq}}) = -8.3144 \cdot 298.15 \cdot \ln(2.906 \cdot 10^{-11}) = 60 \dots \text{kJ/mol},$$

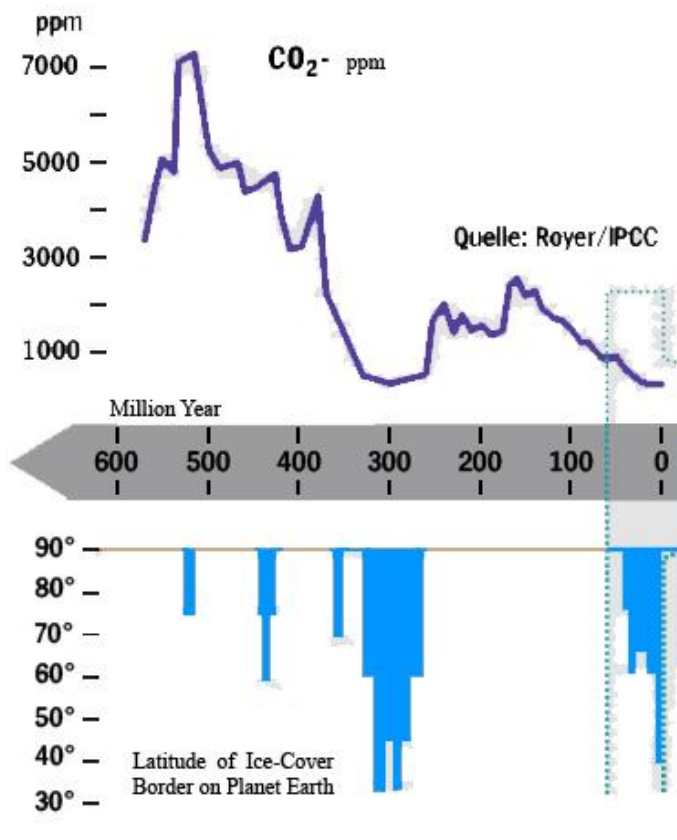
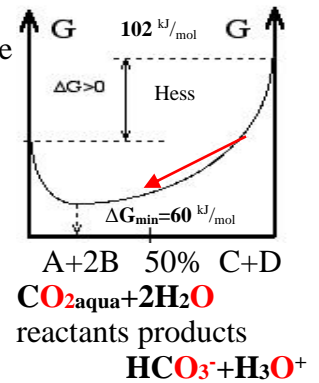
Endothermic and endoergic  $\text{CO}_{2\text{aq}}$  hydrolysis Hess free energy change  $\Delta G_{\text{hydrolysis}}$  positive 102  $\dots \text{kJ/mol}$ , but minimized in mixture  $\Delta G_{\text{eq}} = 60 \dots \text{kJ/mol}$  reaching

$$\text{equilibrium } \text{K}_{\text{eq}} = \frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}} \cdot [\text{H}_2\text{O}]^2} = 2.906 \cdot 10^{-11} \dots \text{Classic constant}$$

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

principle is Prigogine attractor for Free energy change minimum  $\Delta G_{\text{min}}$  reaching at equilibrium. Free energy change minimum reaching establishes 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  $-20.95 \cdot 10^{17} \text{ kJ}$ , heat of 6.55 Gt evolved warm 10 times less  $1.73 \cdot 10^{17} \text{ kJ}$ .



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 insufficiency 500 MY, 200 MY and new sufficient 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<sup>-</sup></b> <sub>aqua</sub>	-167,08	56,60	<b>-183,955</b>
<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

CRC 2010

$$\Delta G_{\text{Cl}^-} = \Delta H_{\text{H}^-} - T \cdot \Delta S_{\text{H}^-} = -167,08 - 298,15 \cdot 0,0566 = -183,955 \text{ kJ/mol};$$



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

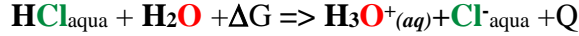
$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{HCl aqua}} - \Delta S^\circ_{\text{HCl gas}} = 56,5 - 186,902 = -130,402 \text{ J/mol/K};$$

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

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

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

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



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

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

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

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

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

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

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

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

37% **HCl** mass in litre solution  $1180 \cdot 0,37 = 436,6 \dots \dots$  g. Mols  $n_{\text{HCl}} = 436,6 \text{ g} / 36,45 = 11,978 \dots \dots$  mol

Water mass in litre solution  $m_{\text{H}_2\text{O}} = 1180 - 436,6 = 743,4 \dots \dots$  g. Number of mols  $n_{\text{H}_2\text{O}} = 743,4 / 18 = 41,3 \dots \dots$  mol

First solution:  $[\text{H}_2\text{O}] = 41,3$ ;  $[\text{H}_3\text{O}^+]_{\text{aq}} = 41,3 - 0,25235 = 41,04765 \dots \dots$  mol/L;  $C_{\text{HCl}} = [\text{HCl}]_{\text{aqua}} + [\text{Cl}^-] = 11,98 \dots \dots$  M;

$$[\text{HCl}]_{\text{aqua}} = (11,978 - 0,25235) = 11,725664 \dots \dots \text{ mol/L};$$

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

As  $[\text{Cl}^-]_{\text{aqua}} = [\text{H}_3\text{O}^+]_{\text{aq}}$  and replacing  $[\text{Cl}^-]_{\text{aqua}}$  wiyh  $[\text{H}_3\text{O}^+]_{\text{aq}}$  square equation is solved as:  $ax^2 + bx + c = 0$ .

$$(11,978 - [\text{Cl}^-]) [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+] \cdot [\text{Cl}^-]_{\text{aqua}}; (11,978 - [\text{H}_3\text{O}^+]) [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{O}^+];$$

$$[\text{H}_3\text{O}^+]^2 + [\text{H}_2\text{O}] \cdot K_{\text{dis}} \cdot [\text{H}_3\text{O}^+] - K_{\text{dis}} \cdot [\text{H}_2\text{O}] \cdot 11,978 = 0$$

Square equation  $ax^2 + bx + c = 0$  solves real root of two mathematic  $x = 1$  and  $2$

$$[\text{Cl}^-]_{\text{aq}} = [\text{H}_3\text{O}^+]_{\text{aq}} = \frac{-K_{\text{dis}} \cdot [\text{H}_2\text{O}] + \sqrt{(K_{\text{dis}} \cdot [\text{H}_2\text{O}])^2 - 4 \cdot (-K_{\text{dis}} \cdot [\text{H}_2\text{O}] \cdot 11,978)}}{2} = 0,25235 \dots \dots \text{ M}$$

$$[\text{Cl}^-]_{\text{aq}} = [\text{H}_3\text{O}^+]_{\text{aq}} = \left( \frac{-1,323 \cdot 10^{-4} \cdot 41,04765 + \sqrt{(1,323 \cdot 10^{-4} \cdot 41,04765)^2 - 4 \cdot (-1,323 \cdot 10^{-4} \cdot 41,04765 \cdot 11,978)}}{2} \right) = 0,25235 \dots \dots \text{ M}$$

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

$$[\text{H}_3\text{O}^+] = 0,25235 \dots \dots \text{ M} = 10^{-\text{pH}} = 10^{-0,598}; \text{ pH} = -\log[\text{H}_3\text{O}^+]_{\text{aq}} = -\log 0,2523 = 0,598 \dots \dots;$$

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

$$\text{Equilibrium constant } \frac{[\text{H}_3\text{O}^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{HCl}]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = (0,25235 \cdot 0,25235) / (41,0476 \cdot 11,725664) = 1,323 \cdot 10^{-4} \dots \dots$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,0001323) = 22,138 \dots \dots \text{ kJ/mol},$$

Unfavored protolysis Hess law positive: 22,14  $\dots \dots$  kJ/mol, but minimized at equilibrium 22,138  $\dots \dots$  kJ/mol.

Hydro chloric concentration is  $C_{\text{HCl}} = [\text{HCl}]_{\text{aqua}} + [\text{Cl}^-] = 0,1 \text{ M}$ ;  $[\text{H}_2\text{O}] = 53,23 - [\text{H}_3\text{O}^+]_{\text{aq}} = 53,33 - 0,1 = 53,23 \text{ mol/L}$

$$[\text{Cl}^-]_{\text{aq}} = [\text{H}_3\text{O}^+]_{\text{aq}} = \left( \frac{-7,681 \cdot 10^{-4} \cdot 53,2 + \sqrt{(7,681 \cdot 10^{-4} \cdot 53,2)^2 - 4 \cdot (-7,681 \cdot 10^{-4} \cdot 53,2 \cdot 0,1)}}{2} \right) = 0,04729 \dots \dots \text{ M}$$

$$\text{Equilibrium constant } \frac{[\text{H}_3\text{O}^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{HCl}]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = (0,04729 \cdot 0,04729) / (53,2 \cdot 0,05271) = 7,681 \cdot 10^{-4} \dots \dots$$

$$[\text{H}_3\text{O}^+] = 0,04729 \dots \dots \text{ M} = 10^{-\text{pH}} = 10^{-1,325}; \text{ pH} = -\log[\text{H}_3\text{O}^+]_{\text{aq}} = -\log 0,04729 = 1,325 \dots \dots;$$

$$\text{Dissociation degree: } \alpha = C_{\text{dis}} / C_{\text{M}} = 0,04729 / 0,1 = 0,473, \alpha\% = 47,3 \dots \dots \%$$

$$\Delta G_{\text{Hess}} = 22,14 \dots \dots \text{ kJ/mol} \text{ endoergic} \dots \dots \text{ Prigogine minimum } \Delta G_{\text{eq}, 0,1\text{HCl}} = 17,8 \dots \dots \text{ kJ/mol}, 11^{\text{th}} \text{ page:}$$

Ammonia  $\text{NH}_3\text{aq}$  solution protonation and  $\text{NH}_4^+\text{aq}$  protolysis 16<sup>th</sup> page:

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  strong protolytic base  $\text{pK}_b = 4,74 > 9,25 = \text{pK}_a$  weak  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+$ ;

1.  $\text{NH}_3\text{gas} + \Delta G \rightleftharpoons \text{NH}_3\text{aq} + \text{Q}$ ;  $\Delta G_{\text{Hydration}} = \Delta G^\circ_{\text{NH}_3\text{aq}} - \Delta G^\circ_{\text{NH}_3\text{gas}} = 107,5 \dots \text{kJ/mol}$ ;

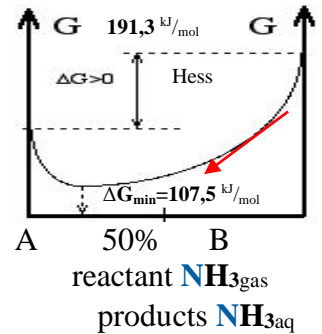
$\Delta G_{\text{Hydration}} = \Delta G^\circ_{\text{NH}_3\text{aq}} - \Delta G^\circ_{\text{NH}_3\text{gas}} = 91,1056 - (-16,4) = 107,5 \dots \text{kJ/mol}$ ;

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

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

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

$K_{\text{eq1}} = \frac{[\text{NH}_3]_{\text{aq}}}{[\text{NH}_3]_{\text{gas}} \cdot [\text{H}_2\text{O}]} = \exp(-\Delta G_{\text{Hess}}/R/T) = \exp(-107500/8,3144/298,15) = 10^{-18,83} \dots$



2.  $\text{NH}_3\text{aq}$  protonation with water strong base  $\text{NH}_3\text{aq} + \text{H}_2\text{O} + \text{Q} \rightleftharpoons \text{NH}_4^+\text{aq} + \text{OH}^- + \Delta G$ ;

$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NH}_4^+} + \Delta H^\circ_{\text{OH}^-} - \Delta H^\circ_{\text{NH}_3} - \Delta H^\circ_{\text{H}_2\text{O}} = -132,5608 - 230,015 - (-132,5 - 285,85) = 55,8 \dots \text{kJ/mol}$  **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
$\text{H}_2\text{O}$	-286,65	-453,188	-151,549
$\text{NH}_4^+\text{aq}$	-132,5	113,4	-79,3
$\text{NH}_3\text{aq}$	-132,5608	-739,2922	91,1056
$\text{NH}_3\text{gas}$	-45,94	192,77	-16,4
$\text{OH}^-$	-230,015	-10,9	-157,2

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

CRC 2010;  $\Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}$

$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}}/T = -55,77/298,15 \cdot 1000 = -187 \text{ J/(mol K)}$ ;

$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_4^+} + \Delta S^\circ_{\text{OH}^-} - \Delta S^\circ_{\text{NH}_3} - \Delta S^\circ_{\text{H}_2\text{O}} = 771,8 \text{ J/mol/K}$ ;

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

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

$\Delta G_{\text{Hess}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 55,77 - 298,15 \cdot 0,7718 = -174,3 \text{ kJ/mol}$ .

$T \cdot \Delta S_{\text{total}} = 0,5848 \cdot 298,15 = 174,4 \text{ kJ/mol}$ ; bound energy;

$\Delta G_{\text{min}} = \Delta G^\circ_{\text{NH}_4^+} + \Delta G^\circ_{\text{OH}^-} - \Delta G^\circ_{\text{NH}_3} - \Delta G^\circ_{\text{H}_2\text{O}} = -79,3 - 157,2 - (91,1056 - 237,191) = -90,4146 \dots \text{kJ/mol}$  **exoergic**

$K_{\text{eq2}} = \exp(-\Delta G_{\text{min}}/R/T) = \exp(90414,6/8,3144/298,15) = 10^{15,84} \dots$ ; favored reaction strong protolytic base.

Hess change negative  $\Delta G_{\text{Hess}} = -286,82 \dots \text{kJ/mol}$  minimized at equilibrium mixture  $\Delta G_{\text{min}} = -90,4 \dots \text{kJ/mol}$ ;

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

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

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

$K_{\text{eq2}} = \frac{[\text{OH}^-]_{\text{aq}} \cdot [\text{NH}_4^+]_{\text{aq}}}{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = 10^{15,84} \dots$  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  $\text{pH} = \text{pK}_a + \log(\frac{n\text{b}\ddot{a}\text{z}\ddot{e}}{n\text{s}\text{k}\ddot{a}\text{b}\ddot{e}})$

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

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

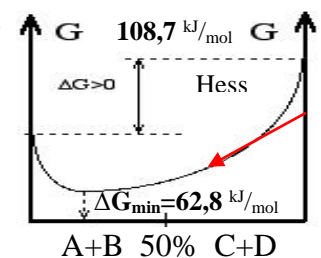
$\Delta G_{\text{Hess}} = \Delta G_{\text{protolysis}} = 108,7 \dots \text{kJ/mol}$  is positive, but minimized to  $\Delta G_{\text{eq}} = 62,8 \dots \text{kJ/mol}$

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

Endothermic and exoergic  $\text{NH}_3\text{aq}$  and  $\text{H}_2\text{O}$  ionization free energy change  $\Delta G_{\text{joniz\ddot{a}c\ddot{i}j\ddot{a}}}$

negative  $-174,3 \dots \text{kJ/mol}$  but minimized to  $\Delta G_{\text{eq2}} = \Delta G_{\text{min}} = -90,4 \dots \text{kJ/mol}$  reactants  $\text{NH}_4^+\text{aq} + \text{H}_2\text{O}$

reaching strong protolytic base equilibrium mixture  $K_{\text{eq2}} = 10^{15,84} \dots$



Le Chatelier principle is Prigogine attractor for Free energy change 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 9<sup>th</sup> [page](#) :

**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  $m_{\text{solution}} = 1203.....\text{g/L}$ .

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

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

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

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

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

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

$[\text{Na}^+_{\text{aq}}] = [\text{Cl}^-_{\text{aq}}] = 49,142/12 = 4,09517 \text{ M}$ . Mass fraction in percents is mass of salt over solution mass

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

Dissociation degree  $\alpha = 4,0952/5,4434 = 75,2\%$  **crystalline NaCl+Q=>Na<sup>+</sup><sub>aq</sub>+Cl<sup>-</sup><sub>aq</sub>+ΔG**; and solubility product is:  $K_{\text{sp}} = K_{\text{eq}} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}_{\text{aq}}] = 4,0952 * 4,0952 / 1,3482 = 12,4393$ , as

Reactant completely converts to products **Na<sup>+</sup><sub>aq</sub>, Cl<sup>-</sup><sub>aq</sub>, NaCl<sub>aq</sub>** free energy change negative:

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

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 : **NaCl<sub>aq</sub> ⇌ Na<sup>+</sup>+Cl<sup>-</sup>** in liter 1000 mL .

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

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

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

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

Disociation degree  $\alpha = 0,98245$  alpha shows non dissociate **[NaCl<sub>aq</sub>]** fraction concentration 0,0027 M:

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

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

$$K_{0,9\%} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}_{\text{aq}}] = 0,15115 * 0,15115 / 0,0027 = 8,4616.....;$$

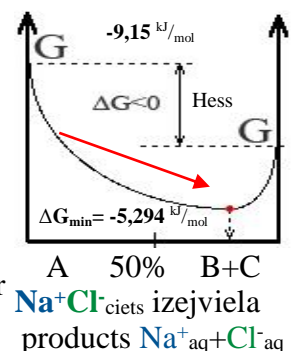
$$\Delta G_{\text{min}1} = \Delta G_{0,9\%} = -R \cdot T \cdot \ln(K_{0,9\%}) = -8,3144 \cdot 298,15 \cdot \ln(8,4616) = -5,294.....\text{kJ/mol},$$

Endothermic and exoergic solubility Hess free energy change  $\Delta G_{\text{Hess}} = -9,15.....\text{kJ/mol}$  is negative, but minimizes  $\Delta G_{\text{min}} = \Delta G_{0,9\%} = -5,294.....\text{kJ/mol}$  in physiologic solution or in saturated solution  $\Delta G_{\text{min}} = \Delta G_{\text{sp}} = -6,25.....\text{kJ/mol}$  reaching equilibrium mixture

$K_{0,9\%} = K_{0,9\%} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}] = 8,4616.....$  or  $K_{\text{sp}} = K_{\text{eq}} = 12,44.....$  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 **Na<sup>+</sup>Cl<sup>-</sup> solubility product** equilibrium mixture.

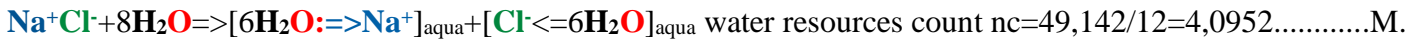


Note: Strong electrolytes are soluble with negative change  $\Delta G < 0$  and greater as one constant  $K_{\text{eq}} \gg 1$  ;

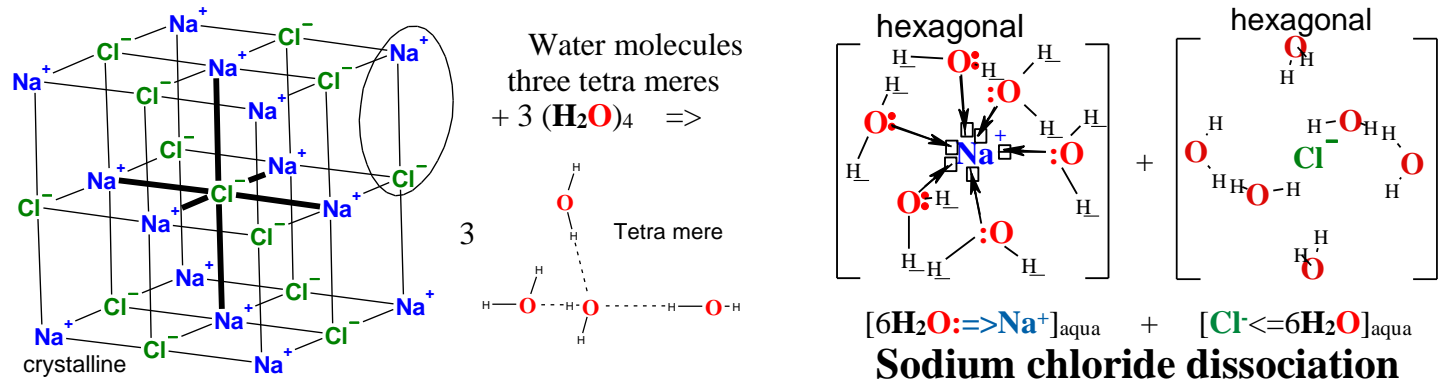
Weak electrolytes with positive change  $\Delta G_{\text{eq}} > 0$  and  $0 < K_{\text{eq}} < 1$  **endoergic** are slightly and like insoluble .



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



$\text{Na}^+\text{Cl}^-$  dissipative disorder three tetra meres  $3(\text{H}_2\text{O})_4$  and ions coordinate six water molecules together 12:



Part  $\text{NaCl}$  remains non dissociate neutral molecules due to insufficient water resources 49,142 mols.

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

$$K_{sp} = [\text{Na}^+_{aq}] * [\text{Cl}^-_{aq}] / [\text{NaCl}_{aq}] = 4,0952^2 / 1,3482 = 12,4393\text{.....};$$

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

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	-
$\text{Cl}^-_{\text{aq}}$	-167,2	56,50	<b>-183,955</b>
$\text{H}_2\text{O}$	-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.....

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

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

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

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \Delta S_{\text{Hess}} = 3,82 - 298,15 * 0,0435 = -9,15\text{.....kJ/mol}$$

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

$$T \cdot \Delta S_{\text{total}} = 30,688 * 298,15 = 9,15\text{.....kJ/mol}$$

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,

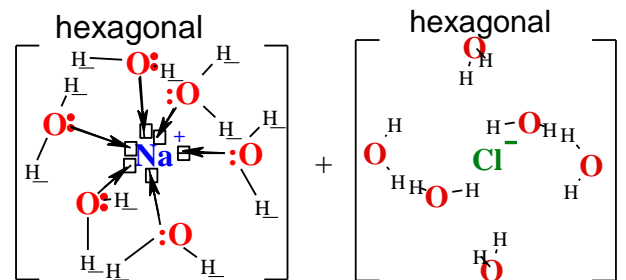
2) Tetra mere  $(\text{H}_2\text{O})_4$  brake ions  $[\text{Na}(\text{H}_2\text{O})_6]^+$ ,  $[\text{Cl}(\text{H}_2\text{O})_6]^-$  hydrate with water molecules in coordination six.

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  $\Delta H_{\text{Hess}} = +3,82 \text{ kJ/mol}$  with cooling. Heat dispersion negative

$\Delta S_{\text{dispersed}} = -12,812 \text{ J/(mol K)}$ , 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  $\Delta H_{\text{Hess}} = \Delta H_{\text{separation}} + \Delta H_{\text{hydration}} = 3,82 \text{ kJ/mol}$  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  $\Delta H_{\text{Hess}} = 3,82 \text{ kJ/mol}$ . It applicate to melting ice mixture, that decrease temperature up to  $-12^\circ \text{C}$ . Freezing cause the

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



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

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

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

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

Amonium chloride mas in litre  $m_{\text{NH}_4\text{Cl}} = 9,7032 * 39,5 \text{ g} = 383,2764$ .....g/L..

Molar mas is sum of atomic mases:  $M_{\text{NH}_4\text{Cl}} = M_{\text{NH}_4} + M_{\text{Cl}} = 14 + 4 + 35,5 = 53,5$ .....g/mol .

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

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

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

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

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

Thermodynamic favored complete dissolution reaction by Hes 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  $\text{NH}_4\text{Cl}_{(s)} + \text{Q} \Rightarrow \text{NH}_4^+_{(aq)} + \text{Cl}^-_{\text{aqua}} + \Delta G_{\text{products}}$ ;

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

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

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

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

endothermic.....

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

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

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

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

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

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

Thermodynamic favored Hess solubility product in water .

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

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

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

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

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

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

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

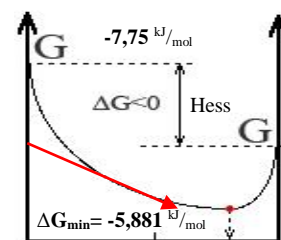
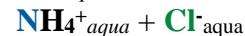
Endothermic and exoergic  $\text{NH}_4\text{Cl}_{(s)}$  dissociation Hess free energy change

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

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

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

reactant non dissociated amonium chloride A 50% B+C  
and products are ions  $\text{NH}_4\text{Cl}_{\text{aqua}}$  A



Le Chatelier principle is Prigogine attractor for Free energy change minimum  $\Delta G_{\text{min}}$  reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium. 13<sup>th</sup> [page](#)

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;  $w\% = 73 \text{ g} / 194,9 \text{ g} * 100\% = 37,455\%$ ;

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

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

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

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

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

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

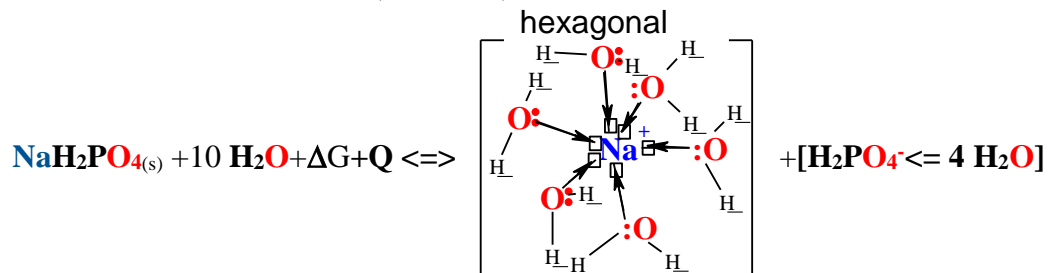
Water  $m_{\text{H}_2\text{O}} = m_{\text{sk}} - m_{\text{NaH}_2\text{PO}_4} = 1320 - 642,73 + 4,12 * 36 = 825,6 \text{ grams}$ ;

$n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 825,59 / 18 = 45,86 \text{ mols}$ .

Saturated solution water coordination resources 7 are enough:  $n_c = n_{\text{H}_2\text{O}} / 10 = 45,866 / 10 = 4,59 \text{ mol}$ .

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.

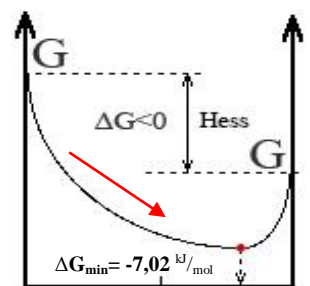
Complete dissociated solubility constant is  $K_{\text{sp\_eq1}} = [\text{Na}^+_{\text{aq}}] * [\text{H}_2\text{PO}_4^-_{\text{aq}}] = 4,12 * 4,12 = 16,9744$

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

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  $\text{NaH}_2\text{PO}_4$  solubility product constant reaction Hess free energy change  $\Delta G_{\text{spHess1}} = \text{?????} \text{ kJ/mol}$  negative (missing data about  $\text{NaH}_2\text{PO}_4$ ), but minimized  $\Delta G_{\text{min}} = \Delta G_{\text{sp\_eq1}} = -7,02 \text{ kJ/mol}$  in mixture reaching solubility product equilibrium

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



In mixture is solid crystalline reactant

A 50% B+C

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

and products

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

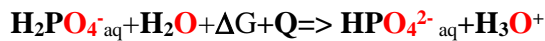
Le Chatelier principle is Prigogine attractor for Free energy change minimum  $\Delta G_{\text{min}}$  reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.





Dihydrogen phosphate deprotonation with water protolysis 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> aqua</b>	-240,1	59	-

CRC 2010

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

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

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

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

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

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

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

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

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

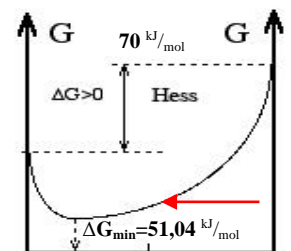
reached equilibrium mixture  $K_{\text{eq}} = \frac{[\text{HPO}_4^{2-}]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = 1,144 \cdot 10^{-9} \dots$

Le Chatelier principle is Prigogine attractor for Free energy change minimum  $\Delta G_{\text{min}}$

reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium. 17<sup>th</sup> [page](#)

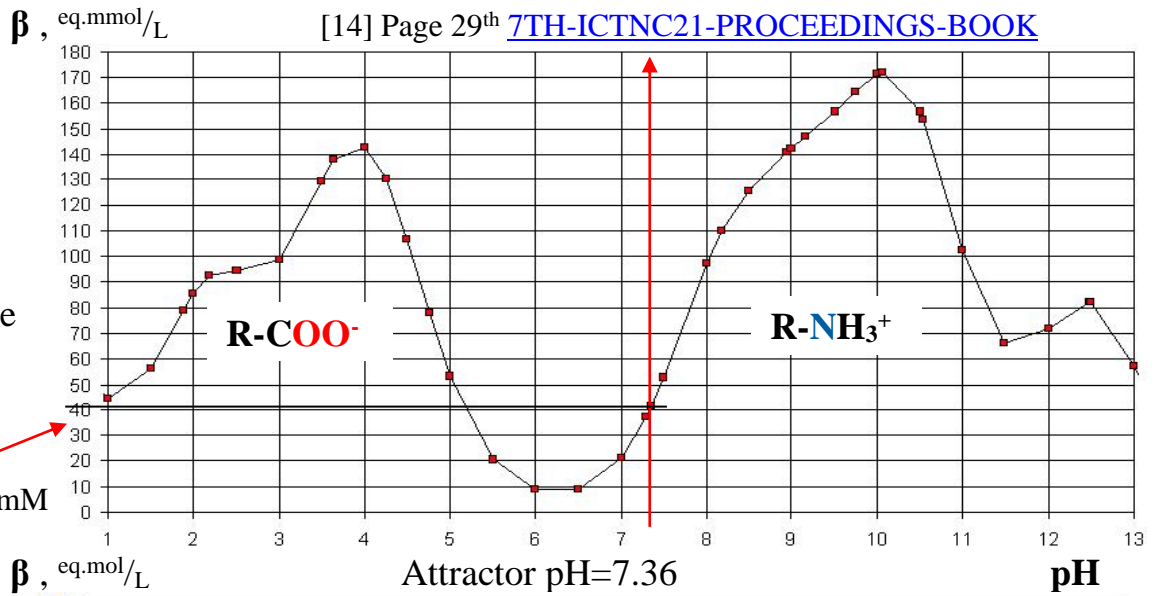
Weak acid unfavored equilibrium friendly to physiologic pH=7,36



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>**.

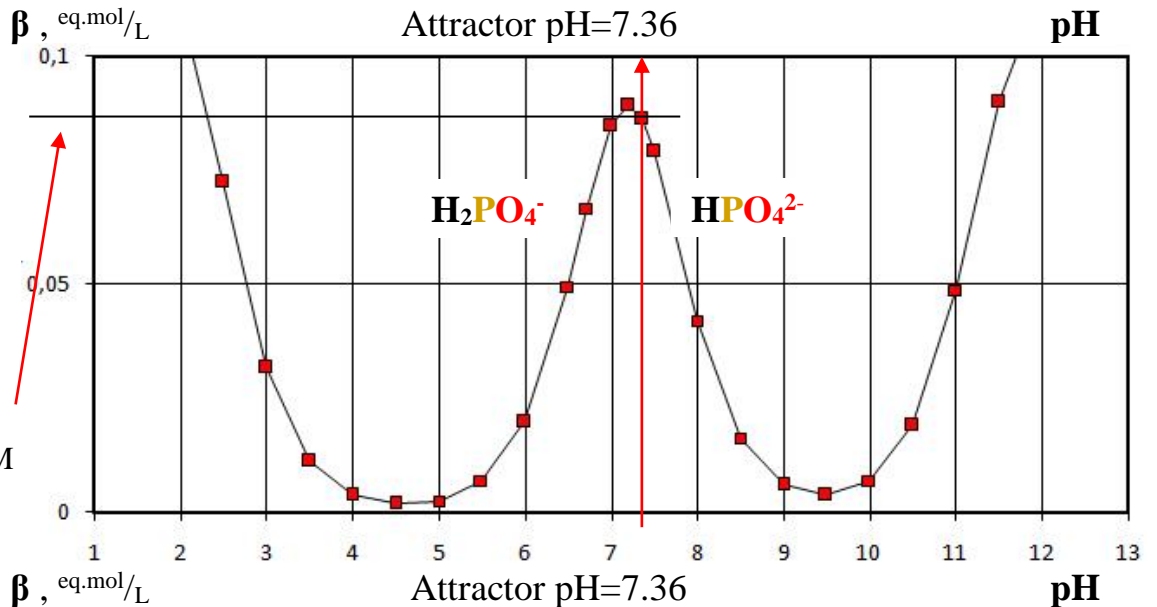


Proteins buffer have silence region from **pH=6** to 7.36. 23 thousand protein total buffer solution concentration is  $C_{buffer}=3 \text{ mM}$ . Muscle cytosol proteins the Buffer capacity at physiologic **pH=7.36** is



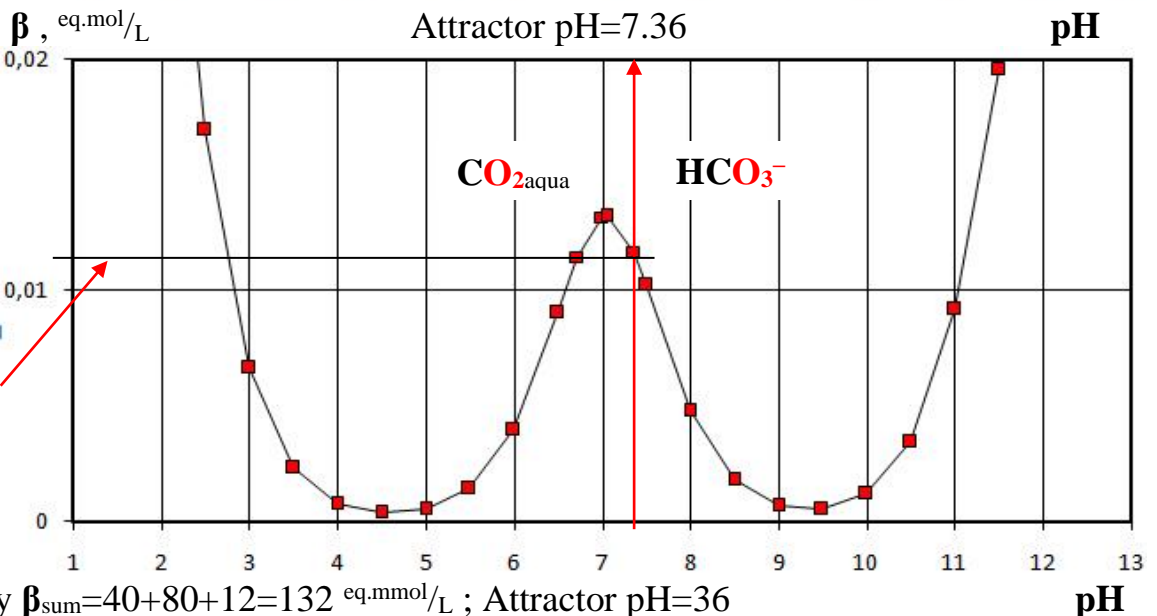
$\beta = 40 \text{ mM}$   
**30.3 %** =  $40/132 * 100\%$

Total phosphate buffer systems concentration  $[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$  in muscle cells cytosol is  $C_{buffer}=0.155 \text{ M}$



The Buffer capacity at physiologic **pH=7.36** is  $\beta = 80 \text{ mM}$   
**66.6 %** =  $80/132 * 100\%$

Total bicarbonate buffer system concentration  $[\text{CO}_{2\text{aqua}}] + [\text{HCO}_3^-]$  is  $C_{buffer}=0.023 \text{ M}$ . The Buffer capacity at physiologic **pH=7.36** is



$\beta = 12 \text{ mM}$   
**9.1 %** =  $12/132 * 100\%$

Total Buffer capacity  $\beta_{sum}=40+80+12=132 \text{ eq.mmol/L}$  ; Attractor pH=36

Figure 3. Cytosol muscle cells. Buffer capacities versus pH values from 1 to 13. Actual buffer capacity at Attractor pH=7.36 for two dominate phosphates , bicarbonate and total protein made buffer capacity sum.

at pH=7.36: proteins + phosphates + bicarbonate,  
 total buffer capacity: 100% = **30.3 %** + **66.6 %** + **9.1 %**;

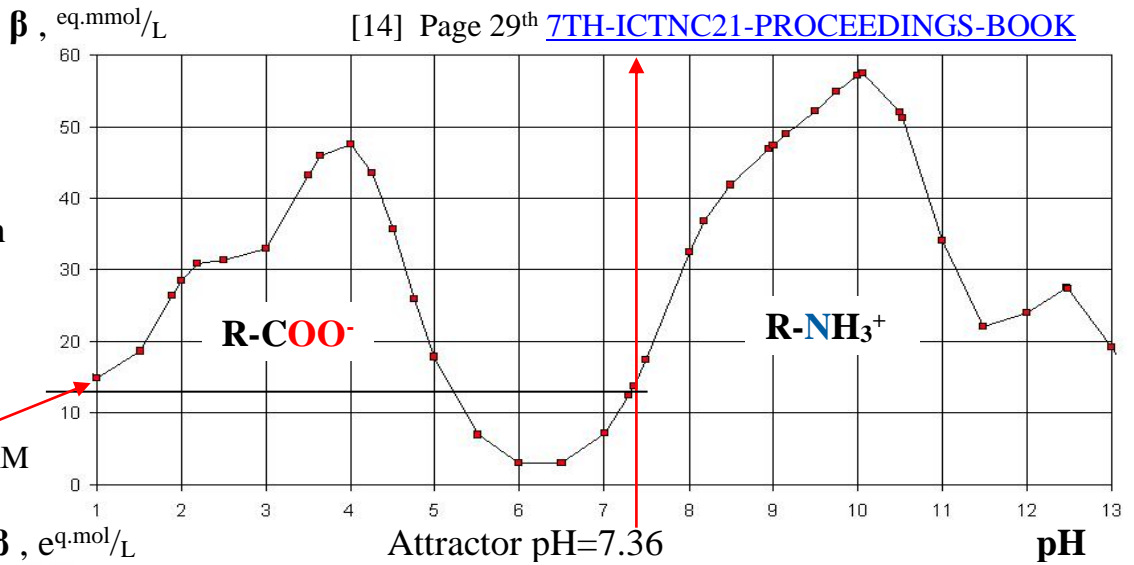
Buffer capacity is acid  $\Delta n_{ac}$  or base  $\Delta n_b$  equivalent\_mols / in one Liter changing pH per one unit  $\Delta \text{pH}=\pm 1$ .

Three buffer systems in human organism by total sum as stabile attractor pH=7.36 create in Cytosol muscle cells functional activity as charged groups. **R-COO<sup>-</sup>**, **R-NH<sub>3</sub><sup>+</sup>**, **HPO<sub>4</sub><sup>2-</sup>**, **R-PO<sub>4</sub><sup>2-</sup>**, **HCO<sub>3</sub><sup>-</sup>**.



Proteins buffer have silence region from **pH=6** to 7.36 . Protein total buffer solution concentration  $C_{buffer}=1$  mM for albumin. The Buffer capacity at physiologic pH=7.36 is

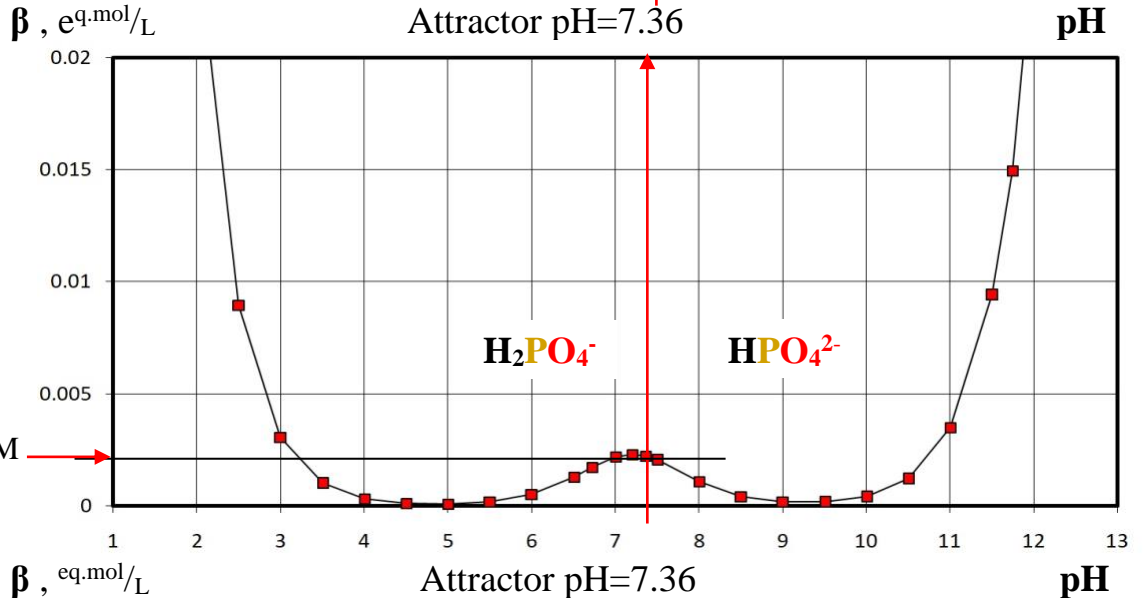
$\beta = 12$  mM  
 $46.15\% = 12/26 * 100\%$



Total phosphate buffer systems concentration  $[H_2PO_4^-] + [HPO_4^{2-}]$  in blood plasma  $C_{buffer}=0.004$  M.

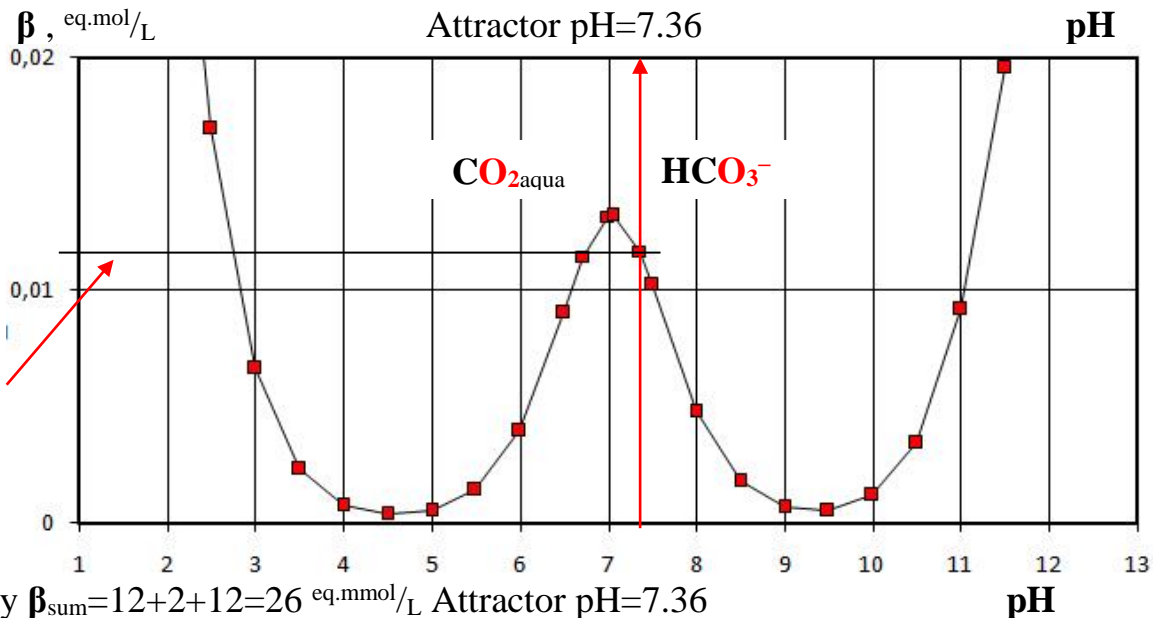
The Buffer capacity at physiologic pH=7.36 is

$\beta = 2$  mM  
 $7.7\% = 2/26 * 100\%$



Total bicarbonate buffer system concentration  $[CO_{2aqua}] + [HCO_3^-]$  in blood plasma is  $C_{buffer}=0.023$  M. The Buffer capacity at physiologic pH=7.36 is

$\beta = 12$  mM  
 $46.15\% = 12/26 * 100\%$



Total Buffer capacity  $\beta_{sum}=12+2+12=26$  eq.mmol/L Attractor pH=7.36

Figure 4. Extra Cellular space Blood plasma. Buffer capacities versus pH values from 1 to 13. Actual buffer capacity at Attractor pH=7.36 for two dominate phosphates , bicarbonate and total protein made buffer capacity sum.

at pH=7.36: proteins + phosphates + bicarbonate ,  
 total buffer capacity: 100% = **46.15%** + **7.7%** + **46.15%**;

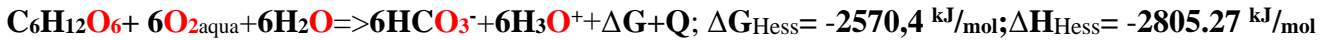
Buffer capacity is acid  $\Delta n_{ac}$  or base  $\Delta n_b$  equivalent\_mols / in one Liter changing pH per one unit  $\Delta pH = \pm 1$ .

Three buffer systems in human organism by total sum as stabile multipurpose Attractor pH=7.36 create in Extra Cellular, Blood plasma functional activity with charged groups **R-COO<sup>-</sup>**, **R-NH<sub>3</sub><sup>+</sup>**, **HPO<sub>4</sub><sup>2-</sup>**, **R-PO<sub>4</sub><sup>2-</sup>**, **HCO<sub>3</sub><sup>-</sup>** as free and linked in amino acids, proteins, nucleic acids, carbohydrates, coenzymes **R** molecules.

## 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 ( $-\text{T} \cdot \Delta\text{S}$ ):

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

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

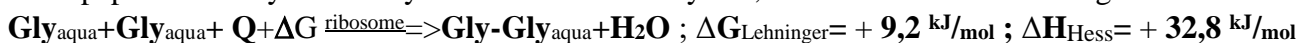
An endothermic reaction of decomposition occurs spontaneously at high enough temperatures.

### 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:  $\text{A} + \text{B} \Rightarrow \text{AB}; \Delta\text{S} < 0$  and  $\Delta\text{H} > 0$ .

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).*

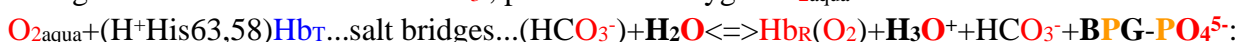
2) *If the direct reaction is spontaneous at high temperatures, the reverse one must be carried out at low temperatures.*

## 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 .

**Shuttle** hemoglobin-based bicarbonate  $\text{HCO}_3^-$ , proton  $\text{H}^+$  to oxygen  $\text{O}_{2\text{aqua}}$  concentration sensitive exchange:



Arterial  $[O_2]=6 \cdot 10^{-5} \text{ M}$   $[Hb_R(O_2)]=0,96$  , venous  $[O_2]= 0,426 \cdot 10^{-5} \text{ M}$   $[Hb_R(O_2)]=0,63$  homeostasis  
 Arterial  $[(H^+)Hb_T \dots \text{salt bridges} \dots (HCO_3^-)]=0,04$  , venous  $[(H^+)Hb_T \dots \text{salt bridges} \dots (HCO_3^-)]=0,37$  .

$$\frac{[Hb_R(O_2)] \cdot [BPG-PO_4^{5-}]}{[(H^+)Hb_T] \cdot [O_2]} = 0,02; 1,2222 \cdot 10^{(-6)} =$$

$K = [Hb_R(O_2)][H_3O^+][HCO_3^-][BPG-PO_4^{5-}] / [(H^+)Hb_T \text{ salt bridges} (HCO_3^-)] / [H_3O^+] / [O_2] = 0,02 \cdot 1,22 \cdot 10^{-6}$  ;  
 arterial  $K = 0,96 \cdot (10^{(-7,36)}) \cdot (0,0154) \cdot 0,005 / 0,04 / 55 / 6 / 10^{(-5)} \leq 0,96 \cdot 0,005 / 0,04 / 6 = 0,02^*$   
 $= (10^{(-7,36)}) \cdot (0,0154) / 10^{(-5)} / 55 = 1,2222 \cdot 10^{(-6)}$ ;

venous  $K = 0,63 \cdot (10^{(-7,36)}) \cdot (0,0154) \cdot 0,005 / 0,37 / 55 / 0,486 / 10^{(-5)} \leq 0,63 \cdot 0,005 / 0,37 / 0,4257 = 0,02$  see level;  
 venous  $K = 0,48 \cdot (10^{(-7,36)}) \cdot (0,0154) \cdot 0,008 / 0,52 / 55 / 0,486 / 10^{(-5)} \leq 0,48 \cdot 0,008 / 0,52 / 0,4333 = 0,02$  mountin;

Circulation in homeostasis generate  $[H^+] = 459 \cdot 6 \cdot 10^{-5} \text{ M} = 0,0275 \text{ M} = [HCO_3^-] = [H^+]$ ;

Normal  $[HCO_3^-] = 0,0154 \text{ M}$ ,  $[CO_{2\text{aqua}}] = 0,0076 \text{ M}$  and  $pH = 7,36$  [Lehninger](#) .[6,], [14] [Page](#) 29<sup>th</sup>.

## 5 complex Enzyme reactions

## Versus non Enzymatic reactions

chaos and contamination

Enzyme governed complexe reactions drive the LIFE in 5 ways

7<sup>th</sup> page : [Velocity KINETICS of REACTION dependence on Attractors create molecules functional Activity](#)

[14] 31<sup>st</sup> [page](#) .

### 1. GRADUAL-CONSECUTIVE organized

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 preceeding in chemistry as side products

### 3. JOINT-TANDEM SYNTHESIS

Ribosomes for polypeptides, proteins  
 Photosynthesis glucose and oxygen

### 3. Thermodynamic forbidden, impossible reaction unfavored has positive free energy change $\Delta G = \Delta H - \Delta S \cdot T > 0$

1<sup>st</sup> 5<sup>th</sup> page:

[Thermodynamic attractor with functionally active  \$O\_{2\text{aqua}}\$ ,  \$CO\_{2\text{aqua}}\$](#)

### 4. COMPETITIVE regulation as inhibition and allostery

sensitive to concentration  $O_{2\text{aqua}}$ ,  $HCO_3^-$ ,  $H^+$  (Le Chatelier principle)

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

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

**4. Chaotic**

so stabilises Physiologic  $pH = 7.36$ , arterial  $[O_{2\text{aqua}}] = 6 \cdot 10^{-5} \text{ M}$  and venous  $[O_{2\text{aqua}}] = 0,426 \cdot 10^{-5} \text{ M}$ .

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

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

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

High rate protolysis attractors  $pH = 7.36 \pm 0,01$ , CA Carbonic Anhydrase,  $H_2O$  stay at equilibrium with functionally activate molecules. These equilibrium states are attractors for non-equilibrium homeostasis states. [4] Generated biochemical environment in dissipative structures present concentration gradients, air 20.95%  $[O_2]$ , osmolar concentration 0,305 M, ionic strength 0,25 M,  $pH = 7,36$ , 310,15 K degree [1], what drive the life irreversible homeostasis. [14]

Organisms are membranes compartmented complex reactions five type enzyme clusters with compounds mixture, in which dissipative structure molecules consuming free energy drive irreversible Brownian molecular engines for evolution and surviving as non-equilibrium homeostasis instruments. [14]

## References.

1. [David R. Lide. CRC Handbook of Chemistry and Physics .90th ed. Taylor and Francis Group LLC; 2010 .](#)
2. Prigogine I, Defey R. Chemical Thermodynamics. Longmans Green & co ©; 1954.
3. Prigogine I, Nicolis G. Self-Organization in Non-Equilibrium Systems. Wiley, 1977.
4. [Prigogine I. Time, Structure and Fluctuations. Lecture, The Nobel Praise in Chemistry; 1977.](#)
5. [Kuman M. New light on the attractors creating order out of the chaos. \*Int J Complement Alt Med.\* \*\*11\*\*\(6\), 337, \(2018\) ;](#)
6. [Nelson DL, Cox MM. Lehninger Principles of Biochemistry. 5<sup>th</sup> ed. New York: W.H. Freeman and company; 2008.](#)
7. [Xing W, Yin G, Zhang J. Rotating Electrode Method and Oxygen Reduction Electrocatalysts. \*Elsevier\*; 6 \(2014\) .](#)
8. [Alberty RA. Biochemical Thermodynamic's : Applications of Mathematics. John Wiley & Sons, Inc. 1-463, \(2006\).](#)
9. [Pinard MA, Mahon B, McKenna R. Probing the Surface of Human Carbonic Anhydrase for Clues towards the Design of Isoform Specific Inhibitors. \*BioMed Research International\*; \*\*2015\*\*, 3 \(2015\).](#)
10. Kotz JC, Purcell KF. Chemistry and chemical reactivity. Saunders College Publishing; 1991.
11. [White VM. THE CARBON CYCLE, ISOTOPES, AND CLIMATE I and II. Lectures 37, 38; 2003 .](#)
12. [Hanania J, Pomerantz C, Stenhouse K, Toor J, Donev J. Carbon cycle. University of Calgary's 2020 .](#)
13. [Der wohltemperierte Planet. \*Der Spiegel.\* 2007 Nr.19:148-154. German .](#)
14. [Kaksis A. The Biosphere Self-Organization Attractors drive perfect order homeostasis reactions to link bioenergetic with functionally activate oxygen and carbon dioxide molecules. 7th International Conference on New Trends in Chemistry September 25-26, 2021.27-32.](#)
15. [Kaksis A. HIGH RATE PROTOLYSIS ATTRACTORS ACTIVATE energy over zero  \$\Delta G\_{H\_2O=CO\_2\(gas\)}=0\$  kJ/mol of water and carbon dioxide. FREE ENERGY CONTENT as BIOSPHERE Self-ORGANIZATION creates PERFECT ORDER IRREVERSIBLE HOMEOSTASIS PROGRESS. 9th International Conference on New Trends in Chemistry 19-21 May, 2023. 14-19.](#)