

## pH calculations

Universal gas constant  $R=8.3144 \text{ J}/(\text{mol}\cdot\text{K})$ ; Faraday's constant  $F=96485 \text{ C}/\text{mol}$ ;  
 $T=310.15 \text{ K}$  (human  $37^\circ \text{ C}$ );  $T=298.15 \text{ K}$  (standard conditions at room temperature  $25^\circ \text{ C}$ ).

EQUATIONS:

- 1)  $\text{pH} = -\lg [\text{H}^+]$ ; 2)  $\text{pOH} = -\lg [\text{OH}^-]$ ; 3)  $\text{pH} + \text{pOH} = 14$ ; 4)  $[\text{H}^+] = 10^{-\text{pH}}$ ; 5)  $[\text{OH}^-] = 10^{-\text{pOH}}$ ;  
 6) strong acids:  $[\text{H}^+] = c_M \cdot \alpha \cdot z$ ; 7)  $\text{pH} = -\log [\text{H}^+] = -\log(c_M \cdot \alpha \cdot z)$ .  
 $\text{H}_2\text{SO}_4 \rightleftharpoons 2 \text{H}^+ + \text{SO}_4^{2-}$  divalent acid has two  $z=2$  hydrogen  $2 \text{H}^+$  cations  
 8) strong bases: 9)  $[\text{OH}^-] = c_M \cdot \alpha \cdot z$ ; 10)  $\text{pH} = -\log [\text{OH}^-] = -\log(c_M \cdot \alpha \cdot z)$ .  
 $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$  divalent base has two  $z=2$  hydroxyl  $2 \text{OH}^-$  ions; weak acids and bases  
**pH** carboxylic, amino, hydrogen phosphate and bicarbonate  $\text{CO}_{2\text{aqua}}$  acid, Ostwald's dilution Law  
 4<sup>th</sup> page : <http://aris.gusc.lv/BioThermodynamics/H2ODissociation.pdf>

Weak acid  $\text{H}_3\text{CCOOH}$ , salt, acetate  $\text{H}_3\text{CCOO}^-$ ; 11)  $K_a = \frac{[\text{H}^+] \cdot [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]_{\text{nondis}}} = 1,74 \cdot 10^{-5} \text{ M}$ .

Protonated amines acid  $\text{NH}_4^+$ , ammoniac base  $\text{NH}_3$ . 12)  $K_a = \frac{[\text{H}^+] \cdot [\text{NH}_3]_{\text{aqua}}}{[\text{NH}_4^+]} = 5,618 \cdot 10^{-10} \text{ M}$ .

Dihydrogen phosphate  $\text{H}_2\text{PO}_4^-$ , hydrogen phosphate  $\text{HPO}_4^{2-}$  13)  $K_a = \frac{[\text{H}^+] \cdot [\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6,3 \cdot 10^{-8} \text{ M}$ .

14)  $\text{pK} = -\lg [K]$ ;  $K = 10^{-\text{pK}}$ ; weak acids 15)  $[\text{H}^+] = \sqrt{K_a \cdot C}$ ; 16)  $\text{pH} = \frac{\text{pK}_a - \log C}{2}$ ;

Amino acids **AA** (aminum acidum)  
 have two type weak acid groups  
 carboxylic and protonated amines:

17)  $K_{a\text{Ca-COOH}} = \frac{[\text{AA-COO}^-] \cdot [\text{H}^+]}{[\text{AA-COOH}]_{\text{nondis}}}$ ; 18)  $K_{a\text{Ca-NH}_3^+} = \frac{[\text{AA-NH}_2] \cdot [\text{H}^+]}{[\text{AA-NH}_3^+]_{\text{protonate}}}$ ;

5<sup>th</sup> page : <http://aris.gusc.lv/BioThermodynamics/H2ODissociation.pdf>

**Osmotic pressure**  $\pi_{\text{osm}}$

21)  $\pi_{\text{osm}} = i \cdot C_M \cdot R \cdot T$ ;  $\pi_{\text{osm}} = C_{\text{osm}} \cdot R \cdot T$ ;

22)  $i = 1 + \alpha (m-1)$ ;  $C_{\text{osm}} = i \cdot C_M$

23)  $[\text{H}^+] = 10^{-\text{pH}} \text{ mol/L}$ ;

24)  $[\text{OH}^-] = 10^{-\text{pOH}} \text{ mol/L}$ ;

25)  $\alpha = \sqrt{\frac{K}{C}}$ ; 26)  $\alpha = \frac{c_{\text{dissoc}}}{c_{\text{total}}}$

$i$  – isotonic coefficient; Vant Hoff's coefficient

$C_M$  – molar concentration - **mol/L**;

$C_{\text{osm}}$  – osmolar concentration - **mol/L**;

$R$  – universal gas constant – **J/mol K**;

$T$  – temperature – **K**;

$\alpha$  – dissociation degree;

$m$  – number of dissociated ions;

**Free energy change  $\Delta G$  in driven process of concentration gradient**

27)  $\Delta G = RT \ln \left( \frac{[\text{HCO}_3^-]_{\text{cytosol}}}{[\text{HCO}_3^-]_{\text{Mitochon}}} \right)$ ,  $\Delta G$  – free energy change in driven process  
 of bicarbonate concentration gradient  $[\text{HCO}_3^-]_{\text{cytosol}}/[\text{HCO}_3^-]_{\text{Mitochon}}$

28)  $\Delta G = RT \ln \left( \frac{[\text{H}_3\text{O}^+]_{\text{extraMembr}}}{[\text{H}_3\text{O}^+]_{\text{Mitochon}}} \right)$ ,  $\Delta G$  – positive free energy accumulation by  
 oxidative phosphorylation driven protons concentration gradient  $[\text{H}_3\text{O}^+]_{\text{extraMembr}}/[\text{H}_3\text{O}^+]_{\text{Mitochon}}$

29)  $\Delta G = RT \ln \left( \frac{C_{\text{outOsm}}}{C_{\text{inOsm}}} \right)$ ,  $\Delta G$  – free energy change by osmosis driven against concentration  
 gradient  $C_{\text{outOsm}}/C_{\text{inOsm}}$  make the pressure  $\pi = \Delta C_{\text{osm}} RT$ , where is positive  $\Delta C_{\text{osm}} = C_{\text{inOsm}} - C_{\text{outOsm}}$

$E_{\text{H}^+\text{-membr}} = P \cdot \log \left( \frac{[\text{H}_3\text{O}^+]_{\text{extraMit}}}{[\text{H}_3\text{O}^+]_{\text{Mitochon}}} \right)$ ;  $E_{\text{HCO}_3^-\text{-membr}} = -P \cdot \log \left( \frac{[\text{HCO}_3^-]_{\text{cytosole}}}{[\text{HCO}_3^-]_{\text{Mitochon}}} \right)$

20)  $\Delta G_F = nF E_{\text{membr\_total}}$ ,  $\Delta G$  – total membrane potential  $E_{\text{H}^+\text{-membr}} + E_{\text{HCO}_3^-\text{-membr}}$ , free energy change  
**[compound]** – molar concentration - **mol/L**;  $C_{\text{osm}}$  – osmo molar concentration - **mol/L**;

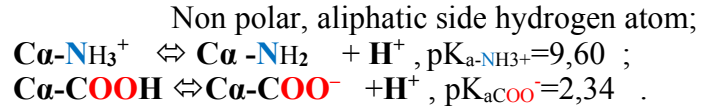
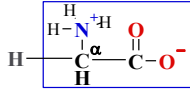
1. To calculate pH<sub>2</sub> of the solution, that was obtained, when to 100 mL of HCl solution having pH<sub>1</sub>=3  
 added 200 mL of H<sub>2</sub>O water.  $C_{M1}=10^{-3} \text{ M}$ ;  $C_{M2}=0.00033 \text{ M}$ ;  $\text{pH}_2=3.48$

2. To V<sub>1</sub> = 1 L liter solution of HNO<sub>3</sub> acid having pH<sub>1</sub> = 0.75 added V<sub>2</sub> = 1 L liter solution of HNO<sub>3</sub> acid  
 having pH<sub>2</sub> = 2. To calculate the pH<sub>3</sub> for obtained solution of strong acid solution !  $C_{M1}=0.178 \text{ M}$ ;  
 $C_{M2}=0.01 \text{ M}$ ;  $C_{M3}=0.09391 \text{ M}$ ;  $\text{pH}_3=1.0273$

3.  $K_{\text{dis}}=3.5 \cdot 10^{-3}$  of a weak acid. To calculate the  $\pi_{\text{osm}}$  osmotic pressure of these solution at  $20^\circ \text{ C}$ , if the  
 $\text{pH}=1.5$  of this solution!  $C_M=0.286 \text{ M}$ ;  $\alpha=0.1107$ ;  $i=1.1107$ ;  $\pi_{\text{osm}}=773.49 \text{ kPa}$

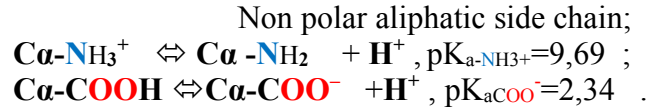
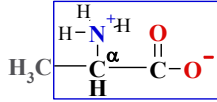
4. Calculate  $pK_{a\_mean}$  of Glycine and what is **pH** attractor friendly with concentration  $C=10^{-8,03}$  mol/L!?

$$pK_{a\_mean}=(2,34+9,6+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,97 + 8,03}{2} = .....!$$



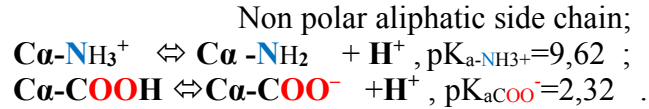
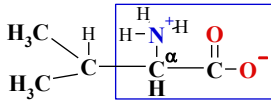
5. Calculate  $pK_{a\_mean}$  of Alanine and what is **pH** attractor friendly with concentration  $C=10^{-7,985}$  mol/L!?

$$pK_{a\_mean}=(2,34+9,69+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{6,015 + 7,985}{2} = .....!$$



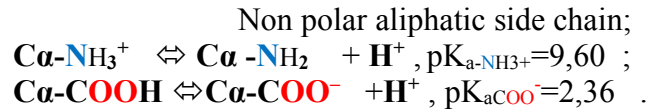
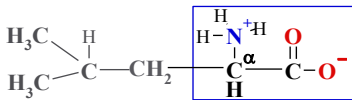
6. Calculate  $pK_{a\_mean}$  of Valine and what is **pH** attractor friendly with concentration  $C=10^{-8,03}$  mol/L!?

$$pK_{a\_mean}=(2,32+9,62+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,97 + 8,03}{2} = .....!$$



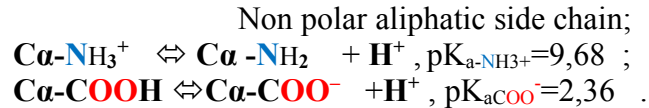
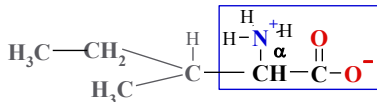
7. Calculate  $pK_{a\_mean}$  of Leucine and what is **pH** attractor friendly with concentration  $C=10^{-8,02}$  mol/L!?

$$pK_{a\_mean}=(2,36+9,60+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,98 + 8,02}{2} = .....!$$



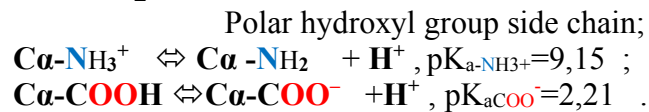
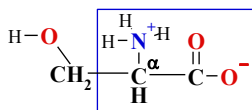
8. Calculate  $pK_{a\_mean}$  of Isoleucine and what is **pH** attractor friendly with concentration  $C=10^{-7,98}$  mol/L!?

$$pK_{a\_mean}=(2,36+9,68+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{6,02 + 7,98}{2} = .....!$$



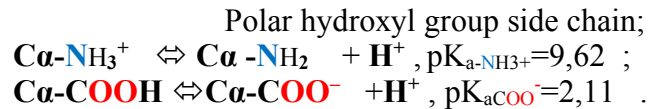
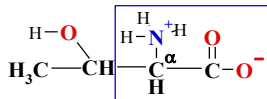
9. Calculate  $pK_{a\_mean}$  of Serine and what is **pH** attractor friendly with concentration  $C=10^{-8,32}$  mol/L!?

$$pK_{a\_mean}=(2,21+9,15+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,68 + 8,32}{2} = .....!$$



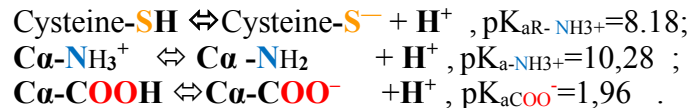
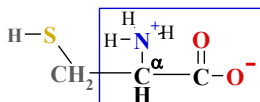
10. Calculate  $pK_{a\_mean}$  of Threonine and what is **pH** attractor friendly with concentration  $C=10^{-8,135}$  mol/L!?

$$pK_{a\_mean}=(2,11+9,62+0)/2=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,865 + 8,135}{2} = .....!$$



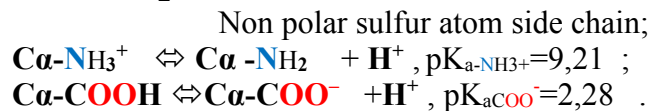
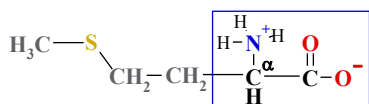
11. Calculate  $pK_{a\_mean}$  of Cysteine and what is **pH** attractor friendly with concentration  $C=10^{-7,193}$  mol/L!?

$$pK_{a\_mean}=(1,96+10,28+8,18)/3=.....; \mathbf{pH} = \frac{pK_{a\_mean} - \log C}{2} = \frac{6,807 + 7,193}{2} = .....!$$



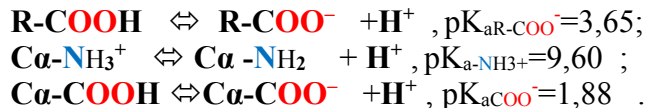
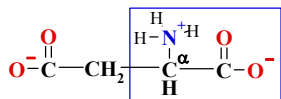
12. Calculate  $pK_{a\_mean}$  of Methionine and what is **pH** attractor friendly with concentration  $C=10^{-8,135}$  mol/L!?

$$pK_{a\_mean} = (2,28+9,21+0)/2 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,865 + 8,135}{2} = \dots\dots!$$



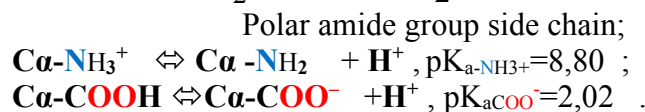
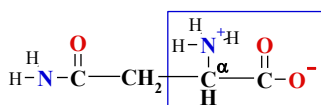
13. Calculate  $pK_{a\_mean}$  of Aspartate and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,957} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (1,88+9,60+3,65)/3 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,043 + 8,957}{2} = \dots\dots!$$



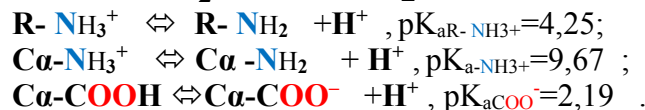
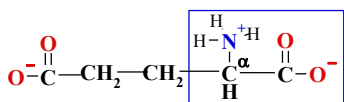
14. Calculate  $pK_{a\_mean}$  of Asparagine and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,59} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (2,02+8,80+0)/2 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,41 + 8,59}{2} = \dots\dots!$$



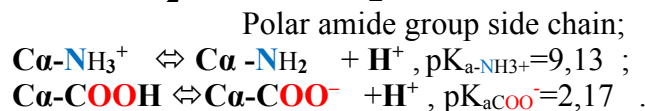
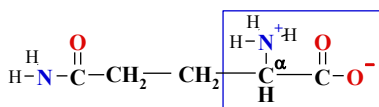
15. Calculate  $pK_{a\_mean}$  of Glutamate and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,63} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (2,19+9,67+4,25)/3 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,37 + 8,63}{2} = \dots\dots!$$



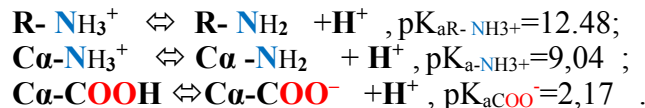
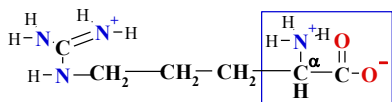
16. Calculate  $pK_{a\_mean}$  of Glutamine and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,35} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (2,17+9,13+0)/2 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,65 + 8,35}{2} = \dots\dots!$$



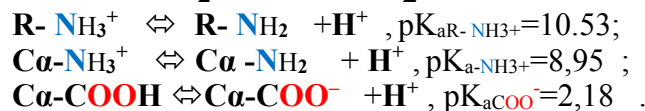
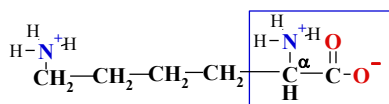
17. Calculate  $pK_{a\_mean}$  of Arginine and what is  $pH$  attractor friendly with concentration  $C = 10^{-6,103} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (2,17+9,04+12,48)/3 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{7,897 + 6,103}{2} = \dots\dots!$$



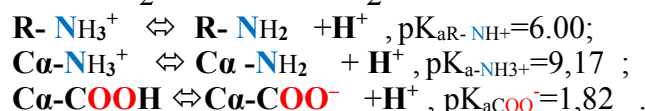
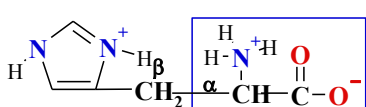
18. Calculate  $pK_{a\_mean}$  of Lysine and what is  $pH$  attractor friendly with concentration  $C = 10^{-6,78} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (2,18+8,95+10,53)/3 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{7,22 + 6,78}{2} = \dots\dots!$$



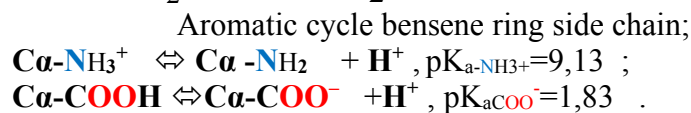
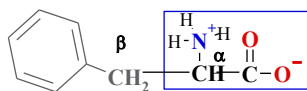
19. Calculate  $pK_{a\_mean}$  of Histidine and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,337} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (1,82+9,17+6,00)/3 = \dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,663 + 8,337}{2} = \dots\dots!$$



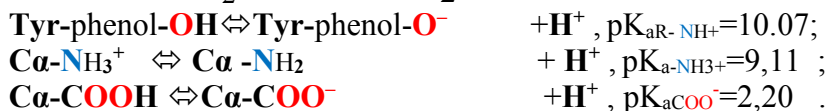
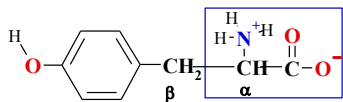
20. Calculate  $pK_{a\_mean}$  of Phenylalanine and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,52} \text{ mol/L}!$ ?

$$pK_{a\_mean} = (1,83+9,13+0)/2 = \dots\dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,48 + 8,52}{2} = \dots\dots!$$



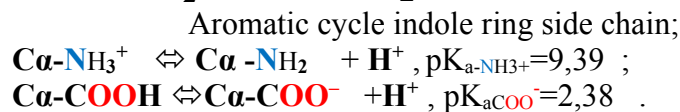
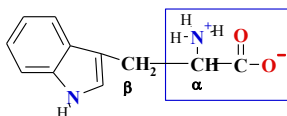
21. Calculate  $pK_{a\_mean}$  of Tyrosine and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,337} \text{ mol/L}$ !?

$$pK_{a\_mean} = (2,20+9,11+10,07)/3 = \dots\dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,663 + 8,337}{2} = \dots\dots!$$



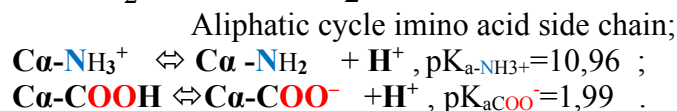
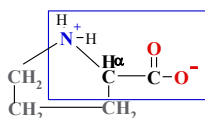
22. Calculate  $pK_{a\_mean}$  of Tryptophan and what is  $pH$  attractor friendly with concentration  $C = 10^{-8,115} \text{ mol/L}$ !?

$$pK_{a\_mean} = (2,38+9,39+0)/2 = \dots\dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{5,885 + 8,115}{2} = \dots\dots!$$



23. Calculate  $pK_{a\_mean}$  of Proline and what is  $pH$  attractor friendly with concentration  $C = 10^{-7,525} \text{ mol/L}$ !?

$$pK_{a\_mean} = (1,99+10,96+0)/2 = \dots\dots\dots; \quad pH = \frac{pK_{a\_mean} - \log C}{2} = \frac{6,475 + 7,525}{2} = \dots\dots!$$



24.  $pH = 2$  and  $K_{dis} = 2 \cdot 10^{-4}$  of a weak acid. To calculate the volume  $V$  in mL of a weak acid that is necessary to take for neutralization of 20 mL 5 % NaOH sodium hydroxide.  $\rho = 1.04 \text{ g/cm}^3$ .

$$(C_{\text{Macid}} = 0.500 \text{ M}; m_{\text{NaOH}} = 1.04 \text{ g}; n_{\text{NaOH}} = 0.026 \text{ mol}; C_{\text{MNaOH}} = 1.30 \text{ M}; V_{\text{acid}} = 52 \text{ mL})$$

25. How much of NaOH sodium hydroxide in g grams have to solute into 500 mL water, that  $pH$  of obtained solution would be  $pH = 12.54$ ,  $\alpha = 90\%$ ,  $M_{\text{NaOH}} = 40 \text{ g/mol}$ .

$$(C_{\text{MNaOH}} = 0.038 \text{ M}; m_{\text{NaOH}} = 0.76 \text{ g};)$$

26.  $pH = 2.08$  of HCl hydrochloric acid solution  $C_{\text{MdisHCl}} = [\text{Cl}^-]_{\text{aq}} = [\text{H}_3\text{O}^+] = 0,008343 = 10^{-2,08} \text{ M}$ , dissociation degree  $\alpha = 83,43\%$ . How many mL are necessary to take for reaction by 100 mL 0.2 M KOH base solution?  $C_{\text{MdisHCl}}/\alpha = 0,008343/0,8343 = C_{\text{MHCl}} = 0,01 \text{ M}$ ;  $n_{\text{KOH}} = 20 \text{ mmol}$ ;

$$V_{\text{HCl}} = n_{\text{KOH}}/C_{\text{MHCl}} = 0,02/0,01 = 2 \text{ mL}; V_{\text{HCl}} = 2 \text{ mL}.$$

27. To calculate  $pH$  of 1.85 % HCl hydrochloric acid solution, if dissociation degree  $\alpha = 80\%$ , and density of solution is  $1 \text{ g/cm}^3$ .  $M_{\text{HCl}} = 36.5 \text{ g/mol}$ . ( $C_{\text{M}} = 0.507 \text{ M}$ ;  $pH = 0.39$ )

28. Osmotic pressure of HCl hydrochloric acid solution at  $0^\circ \text{ C}$  temperature is 454 kPa,  $\alpha = 100\%$ . To calculate  $pH$  of this solution! ( $C_{\text{M}} = 0.099953 \text{ M}$ ;  $pH = 1.00$ )

29.  $pH = 1$  of sulfuric acid  $\text{H}_2\text{SO}_4$  solution, dissociation degree  $\alpha = 50\%$ . To calculate osmotic pressure at  $0^\circ \text{ C}$  temperature of this acidic solution! ( $C_{\text{M}} = 0.100 \text{ M}$ ;  $\pi_{\text{osm}} = 454.23 \text{ kPa}$ )

30. Five liter NaOH solution contains 2 g NaOH. Calculate  $pH$  of solution, if  $\rho = 1 \text{ g/mL}$ ,  $M_{\text{NaOH}} = 40 \text{ g/mol}$ ,  $\alpha = 1$ .  $C_{\text{M}} = 0,01 \text{ mol/L}$ ;  $pH = 12$ .

31.  $pH = 1.5$  of sulfuric acid  $\text{H}_2\text{SO}_4$  solution, dissociation degree  $\alpha = 80\%$ , density  $\rho = 1.05 \text{ g/cm}^3$ . To calculate molarity and mass fraction!

$$(M_{\text{H}_2\text{SO}_4} = 98 \text{ g/mol}; C_{\text{M}} = 0.02 \text{ M}; 1.96\%).$$

32. To calculate molarity of  $\text{Ca}(\text{OH})_2$  calcium hydroxide solution, if

$$\text{pH} = 13.2. \alpha = 90 \%. \quad (C_M = 0.088 \text{ M})$$

33. To calculate the pH of 5 % HCOOH formic acid solution.

$$K_{\text{dis.}, \text{HCOOH}} = 2 \cdot 10^{-4}, \rho = 1.02 \text{ g/cm}^3.$$

$$(m_{\text{acid}} = 51 \text{ g}; M_{\text{HCOOHacid}} = 46 \text{ g/mol}; C_M = 1.1086 \text{ M}; pK_{\text{acid}} = 3.69; \text{pH} = 1.827)$$

34. To calculate the pH of 0.02 M CH<sub>3</sub>COOH acetic acid solution.

$$K_{\text{dis,CH}_3\text{COOH}} = 1.8 \cdot 10^{-5}. (-\log C = 1.7; \text{pH} = 3.22)$$

35. How many times formic acid hydronium ions concentration [H<sub>3</sub>O<sup>+</sup>] grater as the same concentration of acetic acid hydronium ions [H<sub>3</sub>O<sup>+</sup>] concentration?

$$K_{\text{HCOOH}} = 1,77 \cdot 10^{-4}; K_{\text{CH}_3\text{COOH}} = 1,75 \cdot 10^{-5}. [\text{H}_3\text{O}^+] \text{ concentration } 3,18 \text{ times greater....}$$

36. Calculate pH of dihydrogen phosphate and hydrogen phosphate at [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] + [HPO<sub>4</sub><sup>2-</sup>] = 0,155 M sum concentration in distilled water solution, if pK<sub>H<sub>2</sub>PO<sub>4</sub><sup>-</sup></sub> = 7,199 ! Skeletal muscle sell cytosole which are mixed together with other ions: Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and polyelectrolytes of proteins.

$$\text{Answers pH} = 4,0.$$

37. Calculate pH of bicarbonate and CO<sub>2</sub>aqua [HCO<sub>3</sub><sup>-</sup>] + [H<sub>2</sub>O + CO<sub>2</sub>aqua] = 0,027 M sum concentration in distilled water solution, if pK<sub>(H<sub>2</sub>O + CO<sub>2</sub>aqua)</sub> = 7,0512 ! Skeletal muscle sell cytosole which are mixed together with other ions: Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>, Cl<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and polyelectrolytes of proteins..

$$\text{Answers pH} = 4,31.$$

38. Calculate alkaline reserve at [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] + [HPO<sub>4</sub><sup>2-</sup>] = 0,155 M sum of dihydrogen phosphate and hydrogen phosphate buffer solution, if pK<sub>H<sub>2</sub>PO<sub>4</sub><sup>-</sup></sub> = 7,199 ! Answers pH = 1,45 / 1.

$$10^{\text{pH} - \text{pK}_{\text{H}_2\text{PO}_4^-}} = 10^{7,36 - 7,199} = 10^{0,161} = [\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = \dots\dots\dots$$

39. Calculate alkaline reserve at CO<sub>2</sub>aqua at [HCO<sub>3</sub><sup>-</sup>] + [H<sub>2</sub>O + CO<sub>2</sub>aqua] = 0,027 M sum bicarbonate buffer solution, if pK<sub>(H<sub>2</sub>O + CO<sub>2</sub>aqua)</sub> = 7,0512 ! Answers pH = 2 / 1.

$$10^{\text{pH} - \text{pK}_{\text{H}_2\text{O} + \text{CO}_2\text{aqua}}} = 10^{7,36 - 7,0512} = 10^{0,3088} = [\text{HCO}_3^-] / [\text{CO}_2\text{aqua}] = \dots\dots\dots$$

### Student advanced self Studies exercises 40., 41, 42, 43.

Physiologic solution mechanisms maintain balance 7.36 = pH, HCO<sub>3</sub><sup>-</sup>, O<sub>2</sub> in

homeostasis. Human blood 7.36 = pH = -log([H<sub>3</sub>O<sup>+</sup>]), [H<sub>3</sub>O<sup>+</sup>] = 10<sup>-7.36</sup> M = 10<sup>-pH</sup> at stabilized arterial concentration [O<sub>2</sub>aqua] = 6 • 10<sup>-5</sup> M values prevent acidose, hypoxia (deficiency of oxygen) and oxidative stress by metabolism driving H<sub>3</sub>O<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, O<sub>2</sub>aqua

concentration gradients across cell membranes through channels H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, O<sub>2</sub>.

40. Human have pH = 7.4 for blood and is pH = 1.2 value for stomach juice. Human body between blood vessels and stomach cells exists as membranes separated equilibrium between two thermodynamics states for hydrogen ions in blood and in stomach: H<sub>3</sub>O<sup>+</sup><sub>blood</sub> <=Membrane=> H<sub>3</sub>O<sup>+</sup><sub>stomach</sub>.

$$K_{\text{equilibrium}} = [\text{H}_3\text{O}^+]_{\text{stomach}} / [\text{H}_3\text{O}^+]_{\text{Blood}};$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{equilibrium}}) = -2,3 \cdot R \cdot T \cdot \log(K_{\text{equilibrium}})$$

What is the value of equilibrium constant?

Characterize direction in which is equilibrium shifted?

What is value of free energy change ΔG<sub>eq</sub> in this process of one mol H<sub>3</sub>O<sup>+</sup> ion kJ/mol? Which one direction of this flux process via membranes is spontaneous?

$$[\text{H}_3\text{O}^+]_{\text{blood}} = 10^{-7,36} = 3,98 \cdot 10^{-8} \text{ M}; [\text{H}_3\text{O}^+]_{\text{stomach}} = 10^{-1,2} = 6,31 \cdot 10^{-2} \text{ M};$$

$$K_{\text{equilibrium}} = 1,6 \cdot 10^{+6}; \Delta G_{\text{eq}} = -36,77 \text{ kJ/mol}; \text{spontaneous, exoergic...}$$



**41.** Attractors minimised free energy content for one mol of  $O_2$  prevent **acidosis** and **oxidative** stress. Two dominate buffer systems  $pH=7,36$  create constant hydrogen ions concentration  $[H_3O^+]=10^{-7,36}$  M. Water concentration  $[H_2O](37^\circ C)=994.62/18=55,257$  M remarkable decrease power of oxygen. Arterial concentration  $[O_{2,aqua}]=6 \cdot 10^{-5}$  M formed from 20.95% global AIR oxygen  $O_2$  attractor using shuttle  $HCO_3^-$ ,  $H^+ \Leftrightarrow O_{2,aqua}/H_2O$  exchange oxy-deoxy hemoglobin mechanism. At Faraday's  $F=96485$  C/mol and  $R=8.3144$  J/(mol·K) Universal gas constant in expression:  $E_{O_2}=E_{o_{O_2}}+P/4 \cdot \log([O_{2,aqua}] [H_3O^+]^4) = 0.701$  V  $O_{2,aqua} + 4H_3O^+ + 4e^- \Leftrightarrow 6H_2O$ , where constant (310,15 K)  $P$  in volts is :

$$P = \frac{2,3 \cdot R \cdot T}{F} = \frac{\ln(10) \cdot 8.3144 \left( \frac{J}{mol \cdot K} \right) \cdot 310.15(K)}{96485 \left( \frac{C}{mol} \right)} = 0.06154 \dots \text{V. The classic standard potential value}$$

$E_{o_{O_2}} = +1.21865$  V oxygen  $O_2$  has high power diminished for arterial blood  $[O_{2,aqua}]$ ,  $[H^+]=10^{-7,36}$  M

$$E_{O_2} = 1.21865 + 0.06154/4 \cdot \lg([O_{2,aqua}][H^+]^4) = 1.21865 + 0.015385 \cdot \log(6 \cdot 10^{-5} \cdot 10^{-7,36 \cdot 4}) = 0.701 \dots \text{V}$$

and for venous blood concentrations  $[O_{2,aqua}] = 0.426 \cdot 10^{-5}$  M and with  $pH=7,36$  value  $[H^+]=10^{-7,36}$  M

$$E_{O_2} = 1,21865 + 0.06154/4 \cdot \lg([O_{2,aqua}][H^+]^4) = 1.21865 + 0.015385 \cdot \log(0.426 \cdot 10^{-5} \cdot 10^{-7,36 \cdot 4}) = 0.6831 \dots \text{V.}$$

Attractors decrease arterial potential about  $\Delta E_{O_{2,aqua} pH} = E_{O_2} - E_{o_{O_2}} = 0.701 - 1.21865 = -0.51765 \dots \text{V}$  and minimised free energy content for one mol of oxygen per

$$\Delta G_{min} = \Delta E_{O_{2,aqua} pH} \cdot F \cdot n = -0.51765 \cdot 96485 \cdot 4/1000 = -199,8 \dots \text{kJ/mol.}$$

In venous blood potential decreases about  $\Delta E_{O_{2,aqua} pH} = E_{O_2} - E_{o_{O_2}} = 0.6831 - 1.21865 = -0.53555 \dots \text{V}$  and free energy content minimised about  $\Delta G_{min} = \Delta E_{O_{2,aqua} pH} \cdot F \cdot n = -0.53555 \cdot 96485 \cdot 4/1000 = -206,7 \dots \text{kJ/mol.}$

1) Water 55.257 M decreases potential from **1.3795** V to classic 1,21865 V about **-0.16085** V =  $\Delta E_{H_2O}$ .

$$E^{\circ}_{O_2} = E_{o_{O_2}} - 0,06154/4 \cdot \log(1/[H_2O]^6) = 1.21865 - 0.015385 \cdot \log(1/55,257^6) = 1.3795 \dots \text{V ;}$$

Oxidative stress risk potential decrease about  $\Delta E_{H_2O} = E_{O_2} - E^{\circ}_{O_2} = 1.21865 - 1.3795 = -0.16085 \dots \text{V}$  and minimised free energy content for one mol of oxygen about

$$\Delta G_{min} = \Delta E_{H_2O} \cdot F \cdot n = -0,16085 \cdot 96485 \cdot 4/1000 = -62,08 \dots \text{kJ/mol. Total oxidative stress risk arterial decreases for one mol of oxygen about } \Delta G_{min} = \Delta G_{O_{2,aqua} pH} + \Delta G_{H_2O} = -199,8 - 62,08 = -261,88 \dots \text{kJ/mol.}$$

Erythrocytes oxy-deoxy  $O_2$ ,  $HCO_3^-$ ,  $H^+$  shuttle hemoglobin equilibrium from saturation 96% arterial reserves in circulation consume 33% in one liter of blood  $n_{O_2} = 0,02527$  M<sup>mol/L</sup> restoring 459 times arterial based homeostasis concentration  $[O_{2,aqua}] = 6 \cdot 10^{-5}$  M.

Stabilization of  $O_{2,aqua}$ ,  $HCO_3^-$ ,  $H^+$  concentrations prevent acidosis, alkalosis, oxidative stress (hyperoxia with excess) and deficiency - hypoxia. as well as stabilises  $pH 7.36 \pm 0.01$  from arterial  $[O_{2,aqua}] = 6 \cdot 10^{-5}$  M to venous  $[O_{2,aqua}] = 0.426 \cdot 10^{-5}$  M concentration values. Potential arterial

$$E_{O_2} = 0.701 \dots \text{V, } \Delta G_{min} = -199,8 \dots \text{kJ/mol.}, \text{ venous } E_{O_2} = 0.6831 \dots \text{V, } \Delta G_{min} = -206,7 \dots \text{kJ/mol.}$$

Classic standard at  $T=310.15$  K ( $37^\circ$  C) degrees  $E_{o_{O_2}} = 1.21865$  V and thermodynamic  $E_{o_{O_2}} = 1.3795$  V.

Total oxidative stress risk arterial decrease oxygen free energy content  $\Delta G_{min} = -251,82 \dots \text{kJ/mol}$  with attractors  $pH=7,36$  ;  $[H_2O]=55,257$  M ;  $[O_{2,aqua}] = 6 \cdot 10^{-5}$  M (20.95% global AIR oxygen  $O_2$ );

42. What is total membrane potential  $E_{\text{membr\_total}}$  in volts? Calculate the free energy change  $\Delta G_{\text{HCO}_3^-}$  for bicarbonate moving out of mitochondria in kJ/mol!

Physiological active Mitochondria have value of  $\text{pH} = 7.36$  inside and  $\text{pH} = 5$  in extra mitochondrial space. Bicarbonate concentration in cytosole and blood 0,0154 M:

$$[\text{HCO}_3^-] + [\text{CO}_{2\text{aqua}}] = 0.0154 + 0.00757 = \mathbf{0.023M}.$$

Using Henderson Haselbalh equation:

$$\text{pH} = 7.36 = \text{pK} + \log\left(\frac{[\text{HCO}_3^-]_{\text{cytosole}}}{[\text{CO}_{2\text{cytosole}}]}\right), \text{ ratio is alkaline reserve:}$$

$$10^{7.36-7.0512} = \frac{[\text{HCO}_3^-]_{\text{cytosole}}}{[\text{CO}_{2\text{cytosole}}]} = \mathbf{2.036/1} = 0.0154 \text{ M}/0.00757 \text{ M}.$$

In Mitochondria assuming 0.02527 M hemoglobin oxygen reserve used in Krebs cycle the total sum is

$$[\text{HCO}_3^-] + [\text{CO}_{2\text{aqua}}] = \mathbf{0.023M} + \mathbf{0.02527 M} = 0,05054 \text{ M}.$$

As alkaline ratio the same  $10^{7.36-7.0512} = \frac{[\text{HCO}_3^-]}{[\text{CO}_{2\text{aqua}}]} = 2.036/1$ , bicarbonate concentration is:

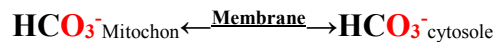
$$[\text{HCO}_3^-] = 2,036 * 0,05054 / (1 + 2,036) = 0,102899 / 3,036 = \mathbf{0,03389...M...}$$

Inside mitochondria bicarbonate concentration is two point two times greater

$$2.2 = \frac{[\text{HCO}_3^-]_{\text{Mitochon}}}{[\text{HCO}_3^-]_{\text{citosols}}} = \mathbf{0.0338919 \text{ M}/0.0154 \text{ M} .}$$

Human body temperature  $t=37^\circ$ ;  $T = 310.15^\circ \text{ K}$ ;  $F=96485 \text{ C/mol}$ ,  $n= -1$  for  $\text{HCO}_3^-$ ....

Actual membrane potential for bicarbonate anions with concentration gradient is:



$$E_{\text{HCO}_3^- \text{ Mitochon}} = -P \cdot \log\left(\frac{[\text{HCO}_3^-]_{\text{cytosole}}}{[\text{HCO}_3^-]_{\text{Mitochon}}}\right) =$$

$$= \mathbf{-0,06154 * \log(0,0154/0,0338919) = 0,02108..... \text{ V}}$$

Actual membrane potential for hydrogen ions  $\text{H}_3\text{O}^+_{\text{Mitochon}} \xleftarrow{\text{Membrane}} \text{H}_3\text{O}^+_{\text{extraMit}} \dots$

$$E_{\text{H}^+ \text{ membr}} = P \cdot \log\left(\frac{[\text{H}_3\text{O}^+]_{\text{extraMit}}}{[\text{H}_3\text{O}^+]_{\text{Mitochon}}}\right) = 0.06154 \cdot \log(10^{-5}/10^{-7.36}) = \mathbf{0.14523..... \text{ V}}$$

Total membrane potential hydrogen and bicarbonate ions is :

$$E_{\text{membr\_total}} = 0.14523 \text{ V} + 0.0210821 = \mathbf{0.1663..... \text{ V};}$$

Membrane potential for bicarbonate, proton gradient as total membrane potential are:

$$E_{\text{HCO}_3^- \text{ Mitochon}} = 0,02108 \text{ V};$$

$$E_{\text{H}^+ \text{ membr}} = 0,14523 \text{ V};$$

$$E_{\text{membr\_total}} = 0.02108 + 0,14523 = 0.1663..... \text{ V};$$

Electric Free energy change for ion  $\text{HCO}_3^-$  negative charge  $n = -1$  is:

$$\Delta G_F = nF E_{\text{membr\_total}} = -1 * 96485 * 0.1663168 = -16.0451..... \text{ kJ/mol exoergic}.$$

Concentration gradient  $\frac{[\text{HCO}_3^-]_{\text{citosol}}}{[\text{HCO}_3^-]_{\text{Mitochon}}}$  made free energy decrease is:

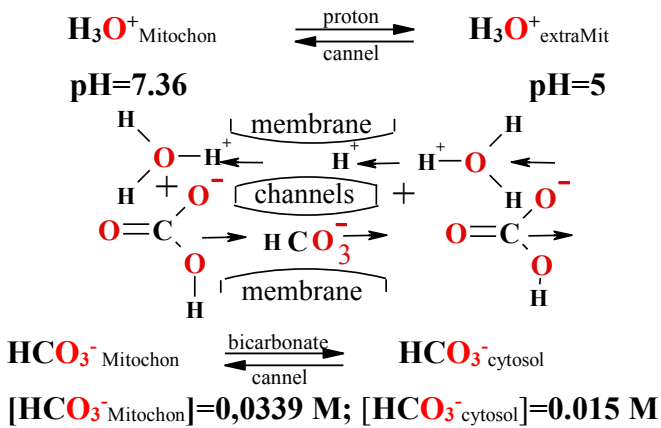
$$\Delta G = RT \ln\left(\frac{[\text{HCO}_3^-]_{\text{citosol}}}{[\text{HCO}_3^-]_{\text{Mitochon}}}\right) =$$

$$= 8.3144 * 310,15 * \ln(0,0154/0,0338919) = -2.0341..... \text{ kJ/mol exoergic}.$$

Bicarbonate total free energy change  $\Delta G_{\text{HCO}_3^-}$  moving out of mitochondria is **exoergic**:

$$\Delta G_{\text{HCO}_3^-} = \Delta G_F + \Delta G = -16.0471 + (-2.0341) = \mathbf{-18.081..... \text{ kJ/mol exoergic}.$$

**43. Mitochondria** Actual membrane potential for hydrogen cations  $\text{H}_3\text{O}^+$  via the membrane proton  $\text{H}^+$  channels and bicarbonate  $\text{HCO}_3^-$  channels reveal the anti parallel (inverse) equilibria:



free energy summary change for concentration gradient through proton  $\text{H}^+$  channels in direction the left to mitochondria crossing lipid bilayer membranes drive the ATPase for synthesis:

$$\leq \Delta G_{\text{membr H}^+} = \Delta G_E + \Delta G_{\text{H}^+} = -30,05846 \text{ kJ/mol}$$

$$\Rightarrow \Delta G_{\text{membr HCO}_3^-} = \Delta G_F + \Delta G_{\text{HCO}_3^-} = -18.081 \text{ kJ/mol}$$

Bicarbonate total free energy change  $\Delta G_{\text{membr HCO}_3^-}$  moving out of mitochondria is **exoergic**:

Hydrogen and bicarbonate total membrane potential is sum of

$$0,14523\text{V} + 0,0210821\text{V} = \mathbf{E_{membr} = 0,1663 \dots \text{V}}$$

Electric free energy change for  $\text{H}^+$  reverse down the potential **0,1663 V**:

$$\Delta G_E = -\mathbf{E_{membr}} \cdot \mathbf{F} \cdot \mathbf{n}_{(\text{ion charge } +1)} = -0,1663 * 96485 * (+1) = -16,045 \dots \text{kJ/mol}$$

Proton move gradient down has minus sign in ATPase channel  $\Delta G_{\text{H}^+} = -RT \ln([\text{H}_3\text{O}^+]_{\text{extraMit}} / [\text{H}_3\text{O}^+]_{\text{Mitochon}}) =$

$$= -RT \ln(10^{-5} / 10^{-7,36}) = -8,3144 * 310,15 * \ln(10^{2,36}) = -14,013 \dots \text{kJ/mol}$$

Free energy summary change for concentration gradient driven through proton  $\text{H}^+$  channels crossing ATPases as ATP synthases the mitochondria lipid bilayer membranes:

$$\Delta G_{\text{membr}} = \Delta G_E + \Delta G_{\text{H}^+} = -16,0454 \text{ kJ/mol} - 14,013 \text{ kJ/mol} = -30,05846 \dots \text{kJ/mol}$$

per one mole of proton  $\text{H}^+$  drive ATPase to make work is 19 times per  $\text{H}_3\text{O}^+$  effective as one mol mass **one gram** of proton  $\text{H}^+$  in direction from extra membrane space ( $\text{H}_3\text{O}^+_{\text{extraMit}}$ ) to mitochondrial matrix space ( $\text{H}_3\text{O}^+_{\text{Mitochon}}$ ).

The proton  $\text{H}^+$  concentration gradient  $\Delta G = \Delta G_{\text{membr}} + \Delta G_{\text{channel}} = -30,058 \dots \text{kJ/mol}$  sum with electrochemical free energy change drive ATPase nano engine to synthesizing ATP molecules. Both free energy negative changes sum per one ATP mole is  $4 * -30,058 \text{ kJ/mol} = \dots \text{kJ/mol}$ , consuming four protons  $4 \text{ H}^+$ , drive ATPase nano engine rotation to synthesizing one  $\text{ATP}^{4-}$  molecule. One mole 503 grams  $\text{ATP}^{4-}$  production have been used 4 grams as four moles of protons. Free energy negative change is  $\Delta G = -120,23 \text{ kJ/mol}$ . ATP bond attractors  $[\text{H}_3\text{O}^+] = 10^{-7,36} \text{ M}$ ,  $[\text{H}_2\text{O}] = 55,257 \text{ M}$  and concentration gradient  $[\text{ATP}^{4-}] / [\text{ADP}^3] = 2,25 / 0,25 = 9$  favoring in human erythrocytes hydrolyze releases free energy  $\Delta G = -55,16 \dots \text{kJ/mol}$  (<http://aris.gusc.lv/BioThermodynamics/BioThermodynamics.doc>: page 22). ATP accumulated chemical free energy efficiency is  $55,16 / 120,2 = \dots \%$  of theoretically consumed 100% ( $-120,23 \text{ kJ/mol}$ ). Oxidative phosphorylation 54,1 % of used four proton chemo osmosis energy consumes the friction of ATPase rotor to heat production and  $\text{ATP}^{4-}$  movement in cytosole water medium forming the concentration gradients across lipid bilayer membranes as transportation free energy source to drive  $\text{ATP}^{4-}$  molecules.

Evidently any other charged cation molecule, for example,  $\text{Na}^+$  cation 23 times heavier or potassium cation  $\text{K}^+$  39 times heavier and its relatively less efficiency per one gram of mass are transferred 23 times or 39 times less energy for  $\text{ATP}^{4-}$  synthesis comparing with charged proton  $\text{H}^+$  transfer through membrane channels.

Life choose the best **small by size** less  $< 0.73 \text{ \AA}$ , **by mass** 1 g / mol and **bearing whole one unit positive charge** proton  $\text{H}^+$ .





## H<sub>2</sub>O Water ionization and neutralization inverse reactions

1. equilibrium  $\text{H}_2\text{O} + \text{H}_2\text{O} + \Delta G^- + Q \Leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ ; 2. equilibrium  $\text{H}_3\text{O}^+ + \text{OH}^- \Leftrightarrow \text{H}_2\text{O} + \text{H}_2\text{O} + \Delta G^- + Q$ ;

Initial compounds and products standard enthalpies and standard entropy values:

<b>H<sub>2</sub>O</b>	$\Delta H^\circ = -286 \text{ kJ/mol}$ ;	$\Delta S^\circ = 69.956 \text{ J/(mol K)}$	$\Delta G = -286 \text{ kJ/mol}$
<b>OH<sup>-</sup></b>	$\Delta H^\circ = -230.00 \text{ kJ/mol}$ ;	$\Delta S^\circ = -10.539 \text{ J/(mol K)}$	
<b>H<sub>3</sub>O<sup>+</sup></b>	$\Delta H^\circ = -285,81 \text{ kJ/mol}$ ;	$\Delta S^\circ = -3,854 \text{ J/(mol K)}$	

Protolysis enthalpy is positive, that indicates heat consuming **Q** from reactants **endothermic**

$$\Delta H_r = \Delta H^\circ_{\text{OH}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - 2\Delta H^\circ_{\text{H}_2\text{O}} = -285,81 - 230 - (2 * (-285,85)) = -515,81 + 571,7 = 55,89 \text{ kJ/mol}$$

2.  $\Delta S_{\text{dispersed}} = -\Delta H_r / T = -55,89 / 298,15 = -187,456 \text{ J/(mol K)}$ . heat accumulates cooling environment.

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

$$2. \Delta S_r = \Delta S^\circ_{\text{OH}^-} + \Delta S^\circ_{\text{H}_3\text{O}^+} - 2\Delta S^\circ_{\text{H}_2\text{O}} = -3,854 - 10,539 - 2 * 69,956 = -14,393 - 139,912 = -154,305 \text{ J/mol/K}$$

Protolysis dissociation free energy change  $\Delta G_r$  is **endoergic, unfavored**

$$\Delta G_r = \Delta H_r - T\Delta S_r = 55,89 + 298,15 * 0,154305 = 101,8967 \text{ kJ/mol}$$

Dissociation is as weak acid in water solution  $K_a = 10^{-17,4868} = 3.26 \cdot 10^{-18}$

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

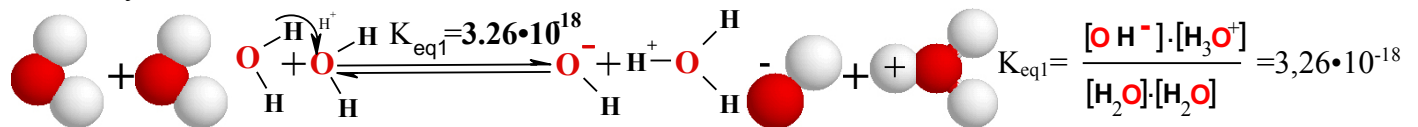
$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -187,456 - 154,305 = -341,761 \text{ J/(mol K)}..$$

Bound free energy in products from environment is negative los of environment:

$$T \cdot \Delta S_{\text{total}} = -341,761 \text{ J/K/mol} \cdot 298,15 \text{ K} = -101,896 \text{ kJ/mol}.$$

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

Thermodynamic unfavored:



$$\Delta G_{\text{eq1}} = -R \cdot T \cdot \ln(K_{\text{eq1}}) = -R \cdot T \cdot \ln\left(\frac{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{O}]}\right) = 99,8 \text{ kJ/mol},$$

Endothermic and endoergic water ionisation reaction Hess free energy

change  $\Delta G_{\text{Hess}} = \Delta G_{\text{protolyse}} = 101,9 \text{ kJ/mol}$  positive, but minimises up to

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 99,8 \text{ kJ/mol}$  reaching equilibrium mixture  $K_{\text{eq1}} = 3.26 \cdot 10^{-18}$

Reaching equilibrium mixture of compounds free energy change

minimises  $99,8 \text{ kJ/mol} = |\Delta G_{\text{eq1}}| < |\Delta G_{\text{Hess1}}| = 101,9 \text{ kJ/mol}$ .

All reactions tend to Prigogine attractor minimum of free energy change

$\Delta G_{\text{min}} = \Delta G_{\text{eq}}$  at equilibrium mixture with inverse constants :

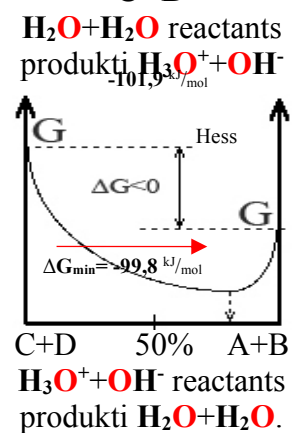
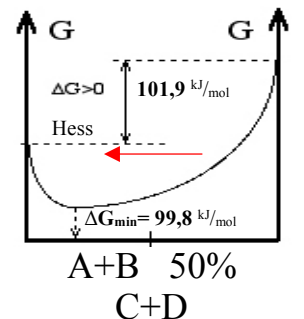
$$3.26 \cdot 10^{-18} = \frac{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{O}]} = K_{\text{eq1}} = \frac{1}{K_{\text{eq2}}} = \frac{1}{\frac{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{O}]}{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}} = \frac{1}{3,068 \cdot 10^{17}}.$$

Note: Multiply with water constant concentration square  $[\text{H}_2\text{O}]^2$

one calculates water ions factorial constant  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

$$K_{\text{eq1}} * [\text{H}_2\text{O}]^2 = 3.26 \cdot 10^{-18} * 55,33^2 = 10^{-14} = K_w = [\text{H}_3\text{O}^+][\text{OH}^-],$$

In 1977 declared Ilya Prigogine attractors create perfect Universe and Science order, as chaos is just apparent.



Ammonia and ammonium ion  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O} + \Delta G + Q \Rightarrow \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+$  protolysis Thermodynamics

CRC 2010

reactants  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O} + \Delta G + Q \Rightarrow \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+$  products  
 endoergic, endothermic

Viela	$\Delta H^\circ_{\text{H}}/\text{kJ/mol}$	$\Delta S^\circ_{\text{H}}/\text{J/mol/K}$	$\Delta G^\circ_{\text{H}}/\text{kJ/mol}$
$\text{H}_3\text{O}^+$	-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>
$\text{NH}_4^+$	-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.  $\Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}$   
 $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NH}_3} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{NH}_4^+} - \Delta H^\circ_{\text{H}_2\text{O}} = 0,901 \dots \text{kJ/mol}$ ;  
 $= -132,5 - 285,81 - (-132,5608 - 286,65) = 0,901 \dots \text{kJ/mol}$  **athermic**.....  
 $\Delta S_{\text{dispersed}} = -\Delta H_{\text{H}}/T = -0,901/298,15 = -3,02 \dots \text{J/(mol K)}$ ;  
 $\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NH}_3} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{NH}_4^+} - \Delta G^\circ_{\text{H}_2\text{O}} = 108,7 \text{ kJ/mol}$ ;  
 $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_3} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{NH}_4^+} - \Delta S^\circ_{\text{H}_2\text{O}} = -403,4 \dots \text{J/mol/K}$ .  
 $= -739,2922 - 3,854 - (113,4 - 453,188) = -403,4 \dots \text{J/mol/K}$ .

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

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

Protolysis enthalpy is positive, that indicates heat consuming **Q** in reactants **endoergic**

Heat accumulates in protolysis products  $\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+$  consuming heat and cooling environment.

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

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

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

Bound free energy in products from environment is negative los of environment:

Thermodynamic constant unfavored:

Ammonium ion  $\text{NH}_4^+$  weak acid  $\text{pK}_a = 9,25$  unfavored equilibrium  $\text{NH}_4^+ + \text{H}_2\text{O} \Rightarrow \text{NH}_{3\text{aq}} + \text{H}_3\text{O}^+$ .

Weak acid  $\text{K}_a = \frac{[\text{H}^+][\text{NH}_3]_{\text{aqua}}}{[\text{NH}_4^+]_{\text{aqua}}} = [\text{H}_2\text{O}] \cdot \text{K}_{\text{eq}} = 55,3 \cdot 1,013 \cdot 10^{-11} = 5,6025 \cdot 10^{-10} = 10^{-9,25} = 10^{\text{pK}_a}$  ;  $\text{pK}_a = 9,25$ ;

Equilibrium constant  $\text{K}_a = \frac{[\text{NH}_3]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = [\text{H}_2\text{O}] \frac{3,26 \cdot 10^{-18}}{1,78 \cdot 10^{-5}} = 55,3 \cdot 1,832 \cdot 10^{-13} = 1,013 \cdot 10^{-11}$

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(\text{K}_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(1,013 \cdot 10^{-11}) = 62,76 \text{ kJ/mol}$ ,

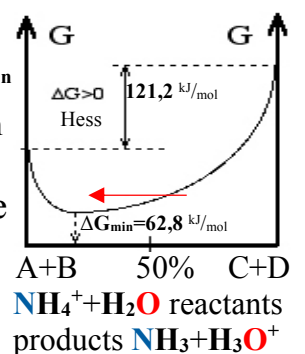
Endothermic and endoergic  $\text{NH}_4^+(\text{aq})$  protolysis reaction free energy change  $\Delta G_{\text{dissociation}}$  positive  $121,2 \text{ kJ/mol}$  , but minimises to  $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 62,76 \text{ kJ/mol}$  reaching equilibrium

in mixture  $\text{K}_a = \frac{[\text{NH}_3]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = 1,013 \cdot 10^{-11}$  . Equilibrium destiny is Prigogine

attractor free energy change minimum  $\Delta G_{\text{min}}$ .

Free energy minimum reaching established equilibrium mixture.

Note: Protonate amines and amino acids are weak acids. Ammonium ions  $\text{NH}_4^+$  are conjugate base ammonia weak acid with constant value  $\text{pK}_a = 9,25$  .



Dihydrogen phosphate  $\text{H}_2\text{PO}_4^-$  protolysis thermodynamic

Data  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  solubility 94,9 g/100g  $\text{H}_2\text{O}$ , density 1,32 g/mL,  $\text{Na}_2\text{HPO}_4$  11,8 g/100g  $\text{H}_2\text{O}$ , density 1,1 g/mL,

CRC 2010 ; BioThermodynamic2006  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} + \Delta G + Q \Rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$  CRC2020; pH=7,36; I=0,25 M;

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>
$\text{H}_3\text{PO}_4$	-1271,7	150,8	-1123,6
$\text{H}_2\text{PO}_4^-$	-1302,6	92.5	-1137,3
$\text{HPO}_4^{2-}$	-1292,14	-33,47	-1089,28
$\text{HPO}_4^{2-}$	<b>-1298,89</b>	<b>-810,792</b>	<b>-1057,143</b>
$\text{PO}_4^{3-}$	-1277,4	-220,5	-1018,7

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

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

$\Delta G_{\text{H}} = \Delta G^\circ_{\text{HPO}_4^{2-}} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{H}_2\text{PO}_4^-} - \Delta G^\circ_{\text{H}_2\text{O}} = 71,936 \dots \dots \dots \text{kJ/mol}$

BioTherm2006;  $= -1089,28 - 213,275 - (-1137,3 - 237,191) = 71,936 \dots \dots \dots \text{kJ/mol}$

1.  $\Delta H_{\text{H}} = \Delta H^\circ_{\text{HPO}_4^{2-}} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_2\text{PO}_4^-} - \Delta H^\circ_{\text{H}_2\text{O}} = 10,5 \text{ kJ/mol}$  endot

$= -1292,14 - 285,81 - (-1302,6 - 285,85) = -1577,95 - 1588,45 = 10,5 \text{ kJ/mol}$

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

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

Protolysis enthalpy is positive, that indicates heat consuming  $Q$  in reactants endothermic . Heat accumulates in protolysis products  $\text{HPO}_4^{2-} + \text{H}_3\text{O}^+$  consuming heat and cooling environment. Protolysis entropy is negative, that indicates endoergic free energy accumulation in products. Protolysis dissociation free energy change  $\Delta G_r$  is **endoergic, unfavored** :

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

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

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

Bound free energy in products from environment is negative los, get out of environment:

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

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

Note: Dihydrogen phosphate  $\text{H}_2\text{PO}_4^-$  aq buffer is one of two dominante in Biochemistry with  $\text{pKa} = 7,199$ .

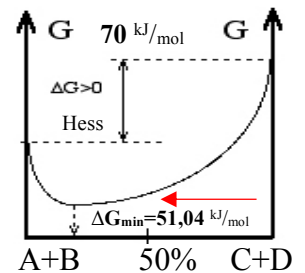
Weak acid equilibrium constant  $\frac{[\text{HPO}_4^{2-}]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = K_{\text{H}_2\text{PO}_4^-} / [\text{H}_2\text{O}] = 10^{-7,199} / 55,3 = 1,144 \cdot 10^{-9}$

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

Endothermic and endoergic  $\text{H}_2\text{PO}_4^-$  protolysis reaction free energy change is

$\Delta G_{\text{dissociation}}$  positive 70 kJ/mol , but  $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 51 \text{ kJ/mol}$  minimises reaching

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



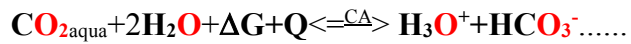
reactants  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$   
products  $\text{HPO}_4^{2-} + \text{H}_3\text{O}^+$

Equilibrium destiny Prigogine attractor is free energy change

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

Enzyme carbonic anhydrase  $\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$  protolysis and  $\text{H}_3\text{O}^++\text{HCO}_3^-$  acid neutralization equilibrium .

Substance	$\Delta H^\circ_{\text{H}}/\text{kJ/mol}$	$\Delta S^\circ_{\text{H}}/\text{J/mol/K}$	$\Delta G^\circ_{\text{H}}/\text{kJ/mol}$
$\text{H}_3\text{O}^+$	-285.81	-3.854	-213,2746
$\text{OH}^-$	-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
$\text{CO}_{2\text{gas}}$	-393,509	213,74	-394,359



1.  $\Delta H_{\text{Hess}}=\Delta H^\circ_{\text{products}}-\Delta H^\circ_{\text{reactants}}$ ; 2.  $\Delta S_{\text{Hess}}=\Delta S^\circ_{\text{products}}-\Delta S^\circ_{\text{reactants}}$   
 3.  $\Delta G_{\text{Hess}}=\Delta H_{\text{Hess}}-T\cdot\Delta S_{\text{Hess}}$ ; **endothermic**.....  
 $\Delta H_{\text{H}}=\Delta H^\circ_{\text{H}_3\text{O}^+}+\Delta H^\circ_{\text{HCO}_3^-}-2\Delta H^\circ_{\text{H}_2\text{O}}-\Delta H^\circ_{\text{CO}_2}=9.7576\dots\dots\text{kJ/mol};$   
 $=-285.81-692,4948-(2\cdot-285.85-413.7976)=9.7576\dots\dots\text{kJ/mol};$   
 $\Delta S_{\text{dispersed}}=-\Delta H_{\text{Hess}}/T=-9,7576/298,15=-32.727\dots\dots\text{J/mol/K};$   
 $\Delta S_{\text{Hess}}=\Delta S^\circ_{\text{H}_3\text{O}^+}+\Delta S^\circ_{\text{HCO}_3^-}-2\Delta S^\circ_{\text{H}_2\text{O}}-\Delta S^\circ_{\text{CO}_2}=-163.0134\dots\dots\text{J/mol/K}$   
 $=-3,854+98,324-(2\cdot69,9565+117,5704)=-163.0134\dots\dots\text{J/mol/K};$   
 $\Delta S_{\text{total}}=\Delta S_{\text{H}}+\Delta S_{\text{dispersed}}=-32.727-163.0134=-195.169\dots\dots\text{J/mol/K};$

Protolysis enthalpy is positive, that indicates heat consuming  $\text{Q}$  in reactants endothermic.

Heat accumulates in protolysis products  $\text{H}_3\text{O}^++\text{HCO}_3^-$  consuming heat and cooling environment.

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

Protolysis dissociation free energy change  $\Delta G_r$  is **endoergic, unfavored** :

$$\Delta G_{\text{Hess}}=\Delta H_{\text{Hess}}-T\cdot\Delta S_{\text{Hess}}=+9.7576+298.15\cdot0.1630134=58.19\dots\dots\text{kJ/mol};$$

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

$$T\cdot\Delta S_{\text{total}}=-195.7404\cdot298,15\text{ K}=-58.19\dots\dots\text{kJ/mol}; \text{ bound } T\Delta S_n \leftarrow \text{accumulated free energy}$$

**endoergic**.....

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

$$\text{Thermodynamic equilibrium } K_{\text{eq}}=\frac{[\text{HCO}_3^-]_{\text{aqua}}\cdot[\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}\cdot[\text{H}_2\text{O}]^2}=\frac{K_{\text{CA}}}{[\text{H}_2\text{O}]^2}=10^{-7,0512}/55,3^2=2,906\cdot10^{-11}.$$

$$\text{Weak acid constant } K_a=K_{\text{eq}}\cdot[\text{H}_2\text{O}]^2=\frac{[\text{HCO}_3^-]_{\text{aqua}}\cdot[\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}}=2,906\cdot10^{-11}\cdot55,3^2=10^{-7,0512}; \text{ p}K_a=7,0512\dots\dots$$

$$\Delta G_{\text{eq}}=-R\cdot T\cdot\ln(K_{\text{eq}})=-8,3144\cdot298,15\cdot\ln(2,906\cdot10^{-11})=60\text{ kJ/mol},$$

Endothermic and endoergic  $\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$  protolysis Hess free energy change is positive  $\Delta G_{\text{dissociation}} 58,2\text{ kJ/mol}$  , but  $\Delta G_{\text{eq}}=60\text{ kJ/mol}$  minimized

$$\text{reaching equilibrium mixture } K_{\text{eq}}=\frac{[\text{HCO}_3^-]_{\text{aqua}}\cdot[\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}\cdot[\text{H}_2\text{O}]^2}=2,906\cdot10^{-11}.$$

Multiplication with water constant concentration  $[\text{H}_2\text{O}]^2=55,3^2\text{ mol/liträ}$ ;

$$K_a=K_{\text{eq}}\cdot[\text{H}_2\text{O}]^2=\frac{[\text{HCO}_3^-]_{\text{aqua}}\cdot[\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}}=10^{-7,0512}.$$

Value  $\text{p}K_a=7,0512$  comes friendly to value  $\text{pH}=7,36$  of homeostasis.

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

Free energy minimum reaching establishes equilibrium mixture.

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

Note:  $\text{pH}=7,36$  is Prigogine attractor to what trend organisms in homeostasis.

