

**pH calculations** <http://aris.gusc.lv/BioThermodynamics/pHaprekiniUzdLd.pdf>

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  $25^\circ \text{ C}$ ).

**KEY EQUATIONS:**

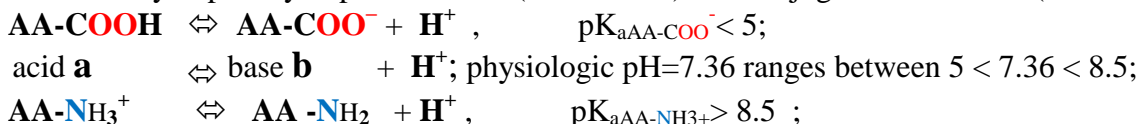
- 1)  $\text{pH} = -\lg [\text{H}^+]$ ; 2)  $\text{pOH} = -\lg [\text{OH}^-]$ ; 3)  $\text{pH} + \text{pOH} = 14$ ; 4)  $[\text{H}^+] = 10^{-\text{pH}}$ ; 5)  $[\text{OH}^-] = 10^{-\text{pOH}}$ ;  
 6) strong acids:  $[\text{H}^+] = c_M \cdot \alpha \cdot z$ ; 7)  $\text{pH} = -\log [\text{H}^+] = -\log(c_M \cdot \alpha \cdot z)$ .  
 $\text{H}_2\text{SO}_4 \rightleftharpoons 2 \text{H}^+ + \text{SO}_4^{2-}$  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  
 $K_a$ - dissociation constant of weak mono valent acid  $\text{H}_3\text{CCOOH}$ , salt (acetate  $\text{H}_3\text{CCOO}^-$ );  
 $K_b$ - dissociation constant of weak mono valent base  $\text{NH}_4\text{OH}$ , ammonium salt (acid  $\text{NH}_4^+$ ).

11)  $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]_{\text{nondis}}}$ ; 12)  $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]_{\text{nondis}}}$ ; 13)  $\text{pK} = -\lg[\text{K}]$ ; 14)  $\text{K} = 10^{-\text{pK}}$ ;  
 15)  $[\text{H}^+] = \sqrt{K_a \cdot C}$ ; 16)  $[\text{OH}^-] = \sqrt{K_b \cdot C}$ ; 17)  $\text{pH} = \frac{\text{pK}_a - \log C}{2}$ ; 18)  $\text{pOH} = \frac{\text{pK}_b - \log C}{2}$ ;

Amino acids **AA** have two type functional groups carboxylic and amino groups:

19)  $K_a = \frac{[\text{AA-COO}^-] \cdot [\text{H}^+]}{[\text{AA-COOH}]_{\text{nondis}}}$ ; 20)  $K_a = \frac{[\text{AA-NH}_2] \cdot [\text{H}^+]}{[\text{AA-NH}_3^+]_{\text{protonated}}}$ ;

The carboxylic protolytic pair an acid **a**( $\text{AA-COOH}$ ) and conjugated base-salt **b**( $\text{AA-COO}^-$ )



Protolytic pair acid **a**( $\text{AA-NH}_3^+$ ) protonated **N** and conjugated base **b**  $\text{AA-NH}_2$  deprotonated **N**.

**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**;

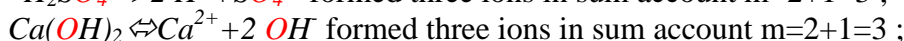
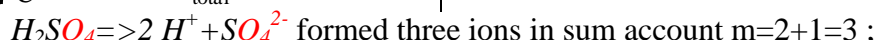
$C_{\text{osm}}$  – osmomolar concentration - **mol/L**;

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

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

29)  $\Delta G = RT \ln(C_{\text{outOsm}}/C_{\text{inOsm}})$ ,  $\Delta G$  – 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  $\Delta C_{\text{osm}} = C_{\text{inOsm}} - C_{\text{outOsm}}$

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

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 pH2 of the solution, that was obtained, when to 100 mL of HCl solution having  $\text{pH}_1=3$  added 200 mL of  $\text{H}_2\text{O}$  water.  $C_{M1}=10^{-3} \text{ M}$ ;  $C_{M2}=0.00033 \text{ M}$ ;  $\text{pH}_2 = 3.48$

2. To  $V_1 = 1 \text{ L}$  liter solution of  $\text{HNO}_3$  acid having  $\text{pH}_1 = 0.75$  added  $V_2 = 1 \text{ L}$  liter solution of  $\text{HNO}_3$  acid having  $\text{pH}_2 = 2$ . To calculate the pH3 for obtained solution of strong acid solution !

$(C_{M1} = 0.178 \text{ M} ; C_{M2} = 0.01 \text{ M} ; C_{M3} = 0.09391 \text{ M} ; \text{pH}_3 = 1.0273)$



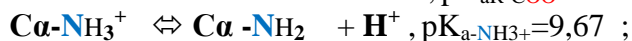
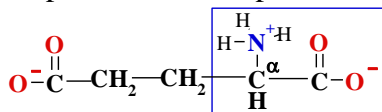
3.  $K_{dis} = 3.5 \cdot 10^{-3}$  of a weak acid. To calculate the  $\pi_{osm}$  osmotic pressure of these solution at 20° C, if the pH = 1.5 of this solution !

$$(C_M = 0.286 \text{ M}; \alpha = 0.1107 ; i = 1.1107 ; \pi_{osm} = 773.49 \text{ kPa})$$

4.  $K_{dis} = 2.2 \cdot 10^{-6}$  of a weak base. To calculate the  $\pi_{osm}$  osmotic pressure of these solution at 0° C, if the pH = 10.5 of this solution !

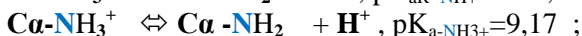
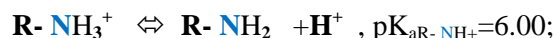
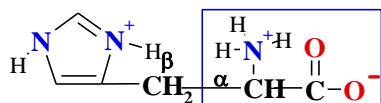
$$(pOH = 3.5 ; C_M = 0.0455 \text{ M}; \alpha = 0.007 ; i = 1.007 ; \pi_{osm} = 103.95 \text{ kPa})$$

5. Calculate dissociation constant  $K_a$  of Glutamate with concentration  $C=0,100 \text{ mol/L}$  and  $pH=3,185!$  Compare it with average constant value  $pK_a=(2,19+9,67+4,25)/3=5,37.....$

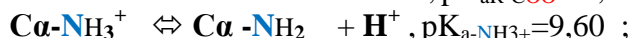
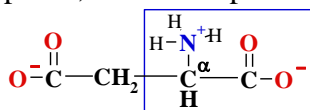


At physiologic  $pH=7,36 \pm 0.01$  carboxylic groups negative charged  $\text{-COO}^-$  and positive amino groups  $\text{-NH}_3^+$  as  $pK$  reference to physiologic  $pH$  value is smaller  $pK_{aR-COO^-} = 4.25 < 7,36$  and  $pK_{aCaCOO^-} = 2,19 < 7,36$  or greater  $7,36 < 9,67 = pK_{aCa-NH_3^+}$  .

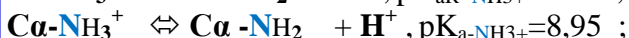
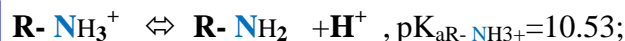
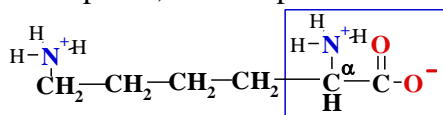
6. Calculate dissociation constant  $K_a$  of Histidine with concentration  $C=0,100 \text{ mol/L}$  and  $pH=3,3315!$  Compare it with average constant value  $pK_a=(1,82+9,17+6,00)/3=5,663.....$



7. Calculate dissociation constant  $K_a$  of Aspartate with concentration  $C=0,100 \text{ mol/L}$  and  $pH=3,0215!$  Compare it with average constant value  $pK_a=(1,88+9,60+3,65)/3=5,043.....$



8. Calculate dissociation constant  $K_a$  of Lysine with concentration  $C=0,100 \text{ mol/L}$  and  $pH=4,11!$  Compare it with average constant value  $pK_a=(2,18+8,95+10,53)/3=7,22.....$



9. Calculate pH of asparagine with dissociation constant  $pK_a=(2,02+8,80)/2=5,41;$

$$K_a = 10^{-5.41} \text{ and } C = 0,3 \text{ mol/L! } pH = \frac{pK_a - \log C}{2} = 2,9664.....$$

10.  $pH = 2$  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.  $\rho = 1.04 \text{ g/cm}^3$ .

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

11.  $pH = 11.2$  and  $K_{dis} = 1.79 \cdot 10^{-5}$  of a weak base. How many mL of 0.1 N HCl hydrochloric acid solution have to take for neutralization of 20 mL basic solution ?

$$(C_{Mbase} = 0.140 \text{ M}; V_{acid} = 28.066 \text{ mL})$$

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

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

13.  $pH = 1.05$  of HCl hydrochloric acid solution, dissociation degree  $\alpha = 80 \%$ . How many mL are necessary to take for reaction by 10 mL 0.2 M KOH base solution ?

$$(C_{Macid} \cdot \alpha = 8.9 \cdot 10^{-2} \text{ N}; C_{Macid} = 0.1114 \text{ M}; n_{base} = 2 \text{ mmol/L}; V_{acid} = 17.95 \text{ mL})$$

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

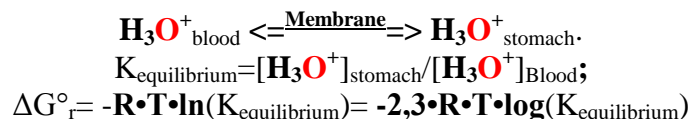
15. Osmotic pressure of HCl hydrochloric acid solution at 0° C temperature is 454 kPa,  $\alpha=100 \%$ . To calculate pH of this solution! ( $C_M = 0.099953 \text{ M}$ ;  $pH=1.00$ )

16. 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!  
 ( $C_M = 0.100\text{M}$ ;  $\pi_{\text{osm}} = 454.23\text{ kPa}$ )
17. The five 5 liter of  $\text{NaOH}$  sodium hydroxide solution contain 2g  $\text{NaOH}$ . To find pH of this solution, if density  $\rho = 1.1\text{ g/cm}^3$ ,  $\alpha = 1$ !  
 ( $M_{\text{NaOH}} = 40\text{g/mol}$ ,  $n_{\text{NaOH}} = 0.05\text{mol}$ ;  $C_{M\text{NaOH}} = 0.01\text{M}$ ;  $\text{pOH} = 2$ ;  $\text{pH} = 12$ )
18. 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!  
 ( $M_{\text{H}_2\text{SO}_4} = 98\text{ g/mol}$ ;  $C_M = 0.02\text{ M}$ ;  $1.96\%$ ).
19. To calculate molarity of  $\text{Ca(OH)}_2$  calcium hydroxide solution, if  
 $\text{pH} = 13.2$ .  $\alpha = 90\%$ . ( $C_M = 0.088\text{ M}$ )
20. To calculate the pH of 5%  $\text{HCOOH}$  formic acid solution.  
 $K_{\text{dis, HCOOH}} = 2 \cdot 10^{-4}$ ,  $\rho = 1.02\text{ g/cm}^3$ .  
 ( $m_{\text{acid}} = 51\text{ g}$ ;  $M_{\text{HCOOHacid}} = 46\text{ g/mol}$ ;  $C_M = 1.1086\text{ M}$ ;  $\text{pK}_{\text{acid}} = 3.69$ ;  $\text{pH} = 1.827$ )
21. To calculate the pH of 0.02 N  $\text{CH}_3\text{COOH}$  acetic acid solution.  
 $K_{\text{dis, CH}_3\text{COOH}} = 1.8 \cdot 10^{-5}$ . ( $-\log C = 1.7$ ;  $\text{pH} = 3.22$ )
20. pH = 0.7 of  $\text{H}_2\text{SO}_4$  sulfuric acid solution,  $\alpha = 50\%$ ,  $\rho = 1.03\text{ g/cm}^3$ . To calculate mass fraction of this solution!  $M_{\text{H}_2\text{SO}_4} = 98\text{ g/mol}$ ! ( $-\log C = 0.7$ ;  $w\% = 1.9\%$ )
21. Extent 400mL of  $\text{H}_2\text{SO}_4$  sulfuric acid solution contains 0.196g of  $\text{H}_2\text{SO}_4$  of pure sulfuric acid. To calculate pH and pOH for this solution!  
 ( $M_{\text{H}_2\text{SO}_4} = 98\text{g/mol}$ ,  $\alpha = 90\%$ . ( $n_{\text{H}_2\text{SO}_4} = 0.002\text{mol}$ ;  $C_M = 0.005\text{M}$ ;  $\text{pH} = 2.045$ )
22. pH = 0 of  $\text{H}_2\text{SO}_4$  sulfuric acid solution,  $\alpha = 70\%$ . To calculate  $C_M$  and  $w\%$ , if  $\rho = 1.18\text{g/mL}$ !  
 ( $1 = C_M \cdot 2 \cdot 0.7 = 1/1.4 = 0.714\text{ M}$ )
23. How many times formic acid hydronium ions concentration  $[\text{H}_3\text{O}^+]$  greater as the same concentration of acetic acid hydronium ions  $[\text{H}_3\text{O}^+]$  concentration?  
 $K_{\text{HCOOH}} = 1,77 \cdot 10^{-4}$ ;  $K_{\text{CH}_3\text{COOH}} = 1,75 \cdot 10^{-5}$ .  $[\text{H}_3\text{O}^+]$  concentration 3,18 times greater

Student advanced self Studies (*Home Work*) exercises 24., 25., 26, 27.

Physiologic solution mechanisms maintain balance  $7.36 = \text{pH}$ ,  $\text{HCO}_3^-$ ,  $\text{O}_2$  in homeostasis. Human blood  $7.36 = \text{pH} = -\log([\text{H}_3\text{O}^+])$ ,  $[\text{H}_3\text{O}^+] = 10^{-7.36}\text{ M} = 10^{-\text{pH}}$  at stabilized arterial concentration  $[\text{O}_{2\text{aqua}}] = 6 \cdot 10^{-5}\text{ M}$  values prevent acidose, hypoxia (deficiency of oxygen) and oxidative stress by metabolism driving  $\text{H}_3\text{O}^+$ ,  $\text{HCO}_3^-$ ,  $\text{O}_{2\text{aqua}}$  concentration gradients across cell membranes through channels  $\text{H}^+$ ,  $\text{HCO}_3^-$ ,  $\text{O}_2$ .

24. 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:



What is the value of equilibrium constant?

Characterize direction in which is equilibrium shifted?

What is value of free energy change  $\Delta G^\circ$  in this process of one mol  $\text{H}_3\text{O}^+$  ion kJ/mol?

Which one direction of this flux process via membranes is spontaneous?

$[\text{H}_3\text{O}^+]_{\text{blood}} = \dots\dots\dots 3.98 \cdot 10^{-8}\text{ M}$ ;  $[\text{H}_3\text{O}^+]_{\text{stomach}} = \dots\dots\dots 6.31 \cdot 10^{-2}\text{ M}$ ; ...

$K_{\text{equilibrium}} = \dots\dots\dots 1.6 \cdot 10^{+6}$  ;  $\Delta G^\circ = \dots\dots\dots -36.77\text{ kJ/mol}$ ; spontaneous...



25. Calculate what is oxygen half reaction potential  $E_{O_2}$  if blood plasma hydrogen exponent is  $pH = 7.36$  and oxygen arterial concentration is  $[O_{2,aqua}] = 6 \cdot 10^{-5} M$ ! At Faraday's constant  $F=96485 C/mol$  ;  $R=8.3144 J/(mol \cdot K)$ ;

Why  $O_2$  concentration in arterial blood avoid of non enzymatic Oxidation reactions? Why value of  $pH=7.36$  prevents acidosis, alkalosis and oxidative stress?

**Human  $O_2$ ,  $HCO_3^-$ ,  $H^+$  shuttle oxy - deoxy HEMOGLOBIN** controlled oxygen concentration  $[O_{2,aqua}]=6 \cdot 10^{-5} M$  is formed from AIR **20.95%** oxygen  $O_2$ . Assuming, that human body temperature is  $t = 37^\circ C$ ;  $T = 310.15^\circ K$  and standard potential value  $E_{o_{O_2}} = +1.21865 V$  shows oxidizer oxygen  $O_2$  very high power. Nernst's potential for half reaction equilibrium  $O_{2,aqua} + 4H_3O^+ + 4e^- \leftrightarrow 6H_2O$  in arterial blood plasma is:

$$E_{O_2} = E_o + P/4 \cdot \log([O_{2,aqua}] [H_3O^+]^4), \text{ where constant } P \text{ in volts is}$$

$$P = \frac{2,3 \cdot R \cdot T}{F} = \frac{\ln(10) \cdot 8.3144 \left(\frac{J}{mol \cdot K}\right) \cdot 310.15(K)}{96485 \left(\frac{C}{mol}\right)} = 0.06154 V,$$

$$\begin{aligned} E_{O_2} &= 1.21865 + 0.06154/4 \cdot \log(6 \cdot 10^{-5} \cdot (10^{-7.36})^4) = 1.21865 + 0.015385 \cdot \log(10^{-4.22185} \cdot 10^{-29.44}) = \dots \\ &= 1.21865 + 0.015385 \cdot \log(10^{-33.6618}) = 1.21865 - 0.015385 \cdot 33.661848 = \dots \\ &= 1.21865 - 0.5117887531 = \mathbf{0.70076V}; \log(1.85 \cdot 10^{-5} \cdot (10^{-7.36})^4) = \log(10^{-4.7328} \cdot 10^{-29.44}) = \dots \\ &= 1.21865 + 0.015385 \cdot \log(10^{-34.1728}) = 1.21865 - 0.525748528 = \mathbf{0.6929 V} \dots \end{aligned}$$

From erythrocytes oxy-deoxy  $O_2$ ,  $HCO_3^-$ ,  $H^+$  shuttle hemoglobin equilibrium ..... reserves  $n_{O_2} = \underline{0,02527 M}$  mol/L in one liter blood ..... 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 destabilization created ... acidose, alkalosis and oxidative stress as excess  $O_{2,aqua}$  and as deficiency - hypoxia..... as well as deviation of  $pH 7.36 \pm 0.01$  and oxygen concentration values....

(arterial  $[O_{2,aqua}]=6 \cdot 10^{-5} M$  and venous  $1.85 \cdot 10^{-5} M$ ) as decreased or increased .....

Potential arterial  $E_{O_2} = \dots \mathbf{0.701 V}$  and venous  $E_{O_2} = \dots \mathbf{0.6929 V}$  below ..... standard value  $E_{o_{O_2}} = +1.21865 V$ ; ....

Answer arterial :  $E_{O_2} = \dots \mathbf{0.701 V}$  and venous  $E_{O_2} = \dots \mathbf{0.6929 V}$



26. 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 **pH = 7.36** inside and **pH = 5** in extra mitochondrial space. Bicarbonate concentration in cytosole and blood 0,0154 M:

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

Using Henderson Haselbalh equation:

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

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

As alkaline reserve in cytosole is known:

$$[\text{HCO}_3^-] = 2.036 * 0.023 / (1 + 2.036) = 0.10289944 / 3.036 = \mathbf{0.0154 \text{ M}}$$

In Mitochondria assuming 0.02527 M hemoglobin oxygen reserve used in Krebs cycle the total sum is  $[\text{HCO}_3^-] + [\text{CO}_{2\text{aqua}}] = \mathbf{0.023\text{M} + 0.02527 \text{ M} = 0,05054 \text{ M}$ .

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

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

Inside mitochondria bicarbonate concentration is two point two times greater

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

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:



$$\text{Answer: } E_{\text{HCO}_3^- \text{ Mitochon}} = -\text{P} \cdot \log([\text{HCO}_3^-]_{\text{cytosole}} / [\text{HCO}_3^-]_{\text{Mitochon}}) = \dots\dots\dots$$

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

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

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

Total membrane potential hydrogen and bicarbonate ions is :

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

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

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

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

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

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

$$\Delta G_{\text{F}} = nF E_{\text{membr\_total}} = -1 * 96485 * 0.1663168 = -16.0451 \dots\dots\dots \text{kJ/mol} \dots\dots$$

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

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

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

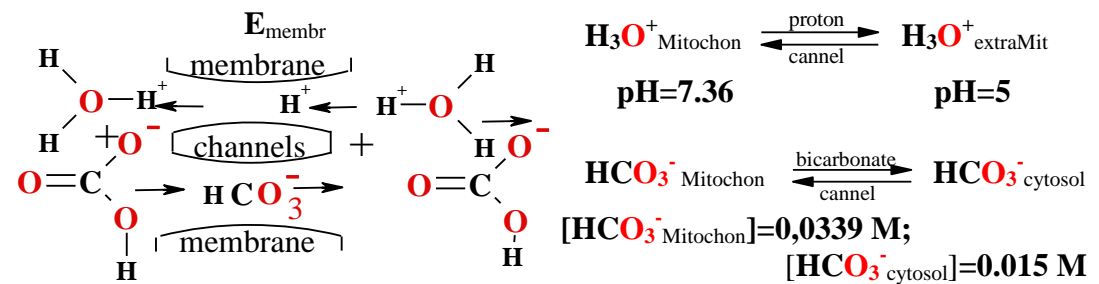
Bicarbonate total free energy change  $\Delta G_{\text{HCO}_3^-}$  moving out of mitochondria is:

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





**27. 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 equilibria:



Hydrogen and bicarbonate total membrane potential is sum of

$$0,14523\text{V}+0.0210821\text{V} = \mathbf{E_{membr}=0,1663\text{V}}.$$

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

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

$$\begin{aligned} \Delta G_{H^+} &= RT \ln \left( \frac{[\text{H}_3\text{O}^+]_{\text{extraMit}}}{[\text{H}_3\text{O}^+]_{\text{Mitochon}}} \right) = \\ &= RT \ln (10^{-5} / 10^{-7,36}) = \mathbf{8,3144} * \mathbf{310,15} * \ln (10^{2,36}) = \mathbf{-14,013 \text{ kJ/mol}} \end{aligned}$$

free energy change for concentration gradient driven through proton  $\text{H}^+$  channels crossing lipid bilayer membranes is the sum:

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

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  $\Delta G = \Delta G_{\text{membr}} + \Delta G_{\text{channel}} = \mathbf{-30,058 \text{ kJ/mol}}$  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

$$4 * \mathbf{-30,058 \text{ kJ/mol}} = \mathbf{-120,232 \text{ kJ/mol}}, \text{ consuming four protons } 4 \text{ H}^+,$$

drive ATPase nano engine rotation to synthesizing one ATP molecule. One mole 503 grams ATP production have been used 4 grams as four moles of protons. Free energy negative change is  $\Delta G = \mathbf{-120 \text{ kJ/mol}}$ . Macro ergic ATP phosphate anhydride bond in hydrolyze releases free energy  $\Delta G = \mathbf{-53.47 \text{ kJ/mol}}$  for human erythrocyte (<http://aris.gusc.lv/BioThermodynamics/BioThermodynamics.doc> page13). For ATP accumulated chemical free energy efficiency is 44,6% ( $\mathbf{-53.47 \text{ kJ/mol}}$ ) of theoretically efficiency 100% ( $\mathbf{-120 \text{ kJ/mol}}$ ). Oxidative phosphorylation 55,4% of used four proton chemo osmose energy consumes the friction of ATPase rotor to heat production and ATP movement in cytosol water medium forming the concentration gradients across lipid bilayer membranes as transportation free energy source to drive ATP 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 ATP synthesis comparing with charged proton  $\text{H}^+$  transfer through membrane channels.

Life choose the best **small by size, by mass and bearing whole one unit positive charge** proton  $\text{H}^+$ .

