Stewart approach to acid base analysis: from concept to practical use

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Take home message

The difference between all methods is how **bicarbonate** is treated!

Traditional method	Base excess	Physicochemical (Stewart)
Bicarbonate (metabolic) Carbon dioxide (respiratory)	Bicarbonate is corrected: Base excess (metabolic)	Bicarbonate is a dependent: • Strong ion difference • Total weak acids • Carbon dioxide

Henderson-Hasselbalch

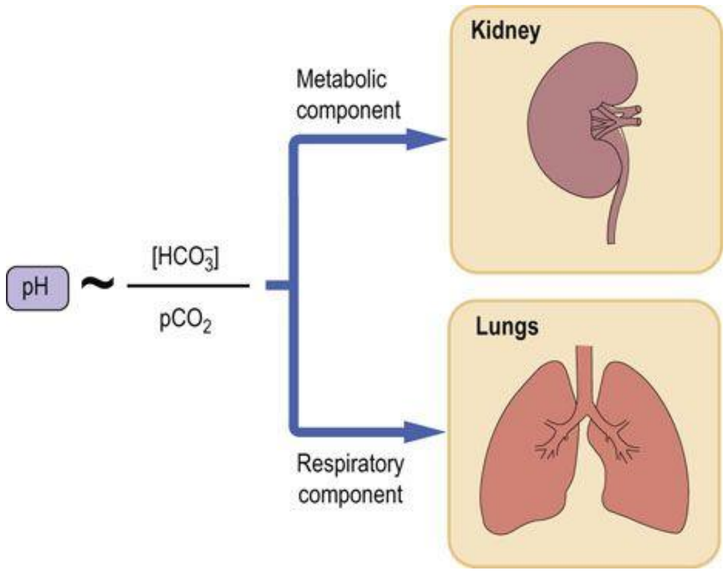
$$pH = pK_a + log_{10}(\frac{[Base]}{[Acid]})$$

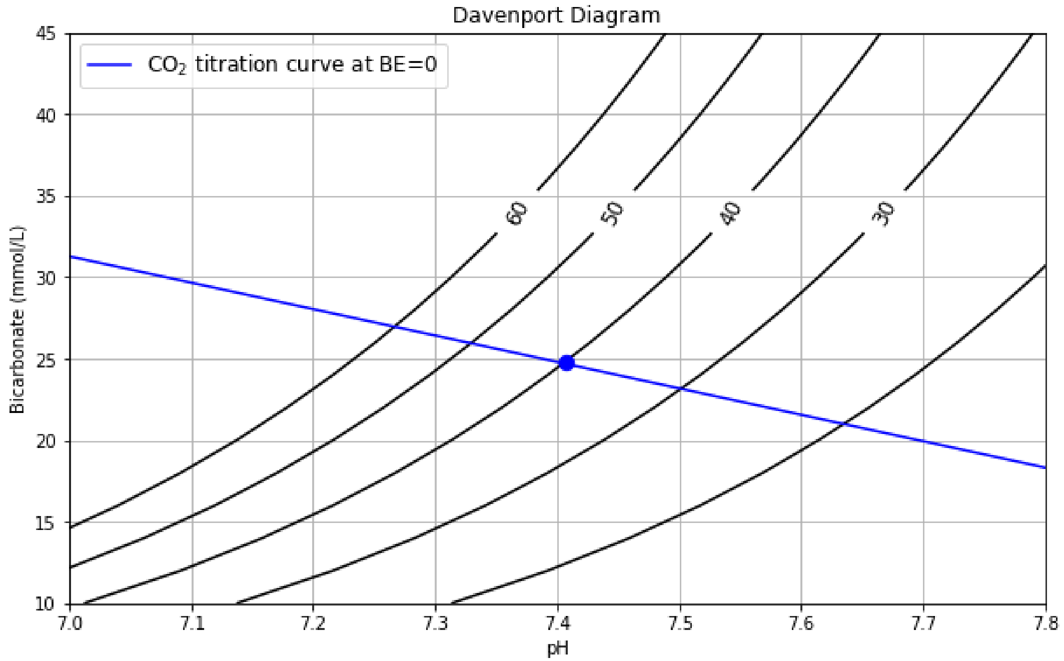
$$CO_2 + H_2O \leftrightarrow \boxed{H_2CO_3 \leftrightarrow HCO_3^- + H^+}$$

- The pH of a solution:
  - Concentration of weak acid
  - Concentration of conjugate base
  - Dissociation constant

$$pH = 6.1 + log \frac{\boxed{HCO_3^-}}{\alpha \times pCO_2}$$

Is bicarbonate a base?



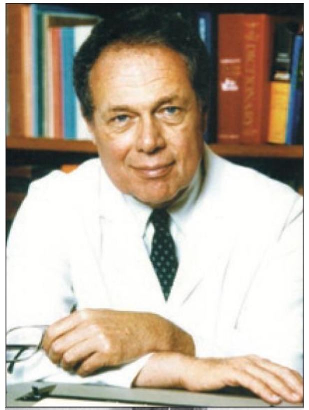


$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

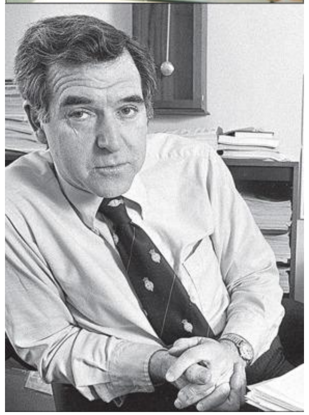
$$BE = (HCO_3^- - 24.8) + (pH - 7.40) \cdot 16.2$$

Δ bicarbonate is not always metabolic

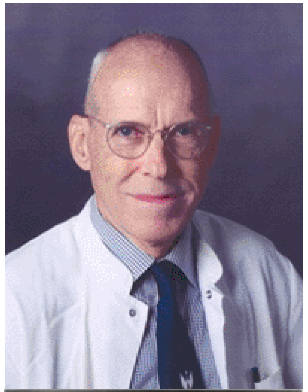
The great transatlantic acid-base debate



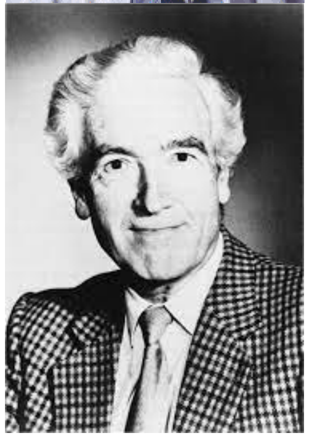
Use the six Boston rules!!



In vitro and oversimplification!!



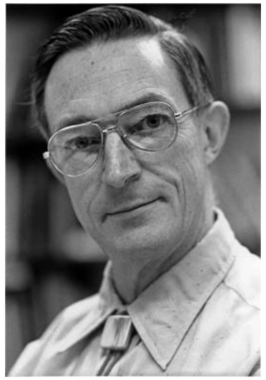
Use a single Danish metabolic marker!!



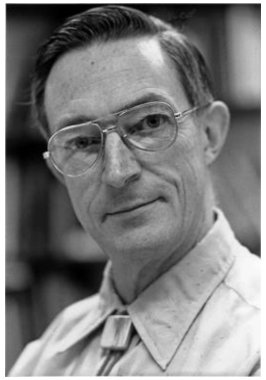
Adjustable and intuitive!!

What is pH, but not why?

- Saline-related acidosis?
- Hypoalbuminemic alkalosis?
- Effect of unmeasured acids?



1977: bring physiochemistry back into an “emotionally charged area of science”



1977: bring physiochemistry back into an "emotionally charged area of science"

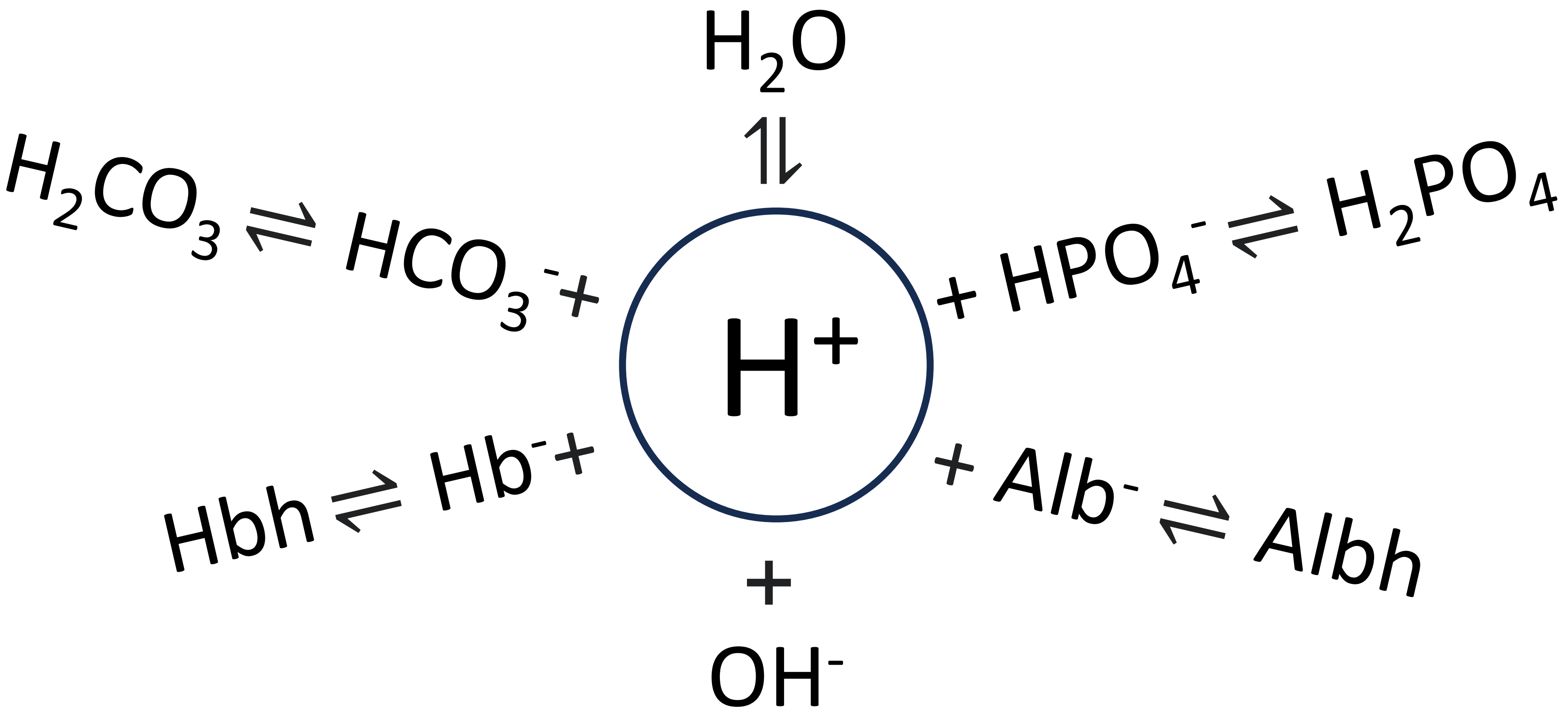
Key contraints

- Dissociation equilibria
- Conservation of mass
- Electrical neutrality

Key players

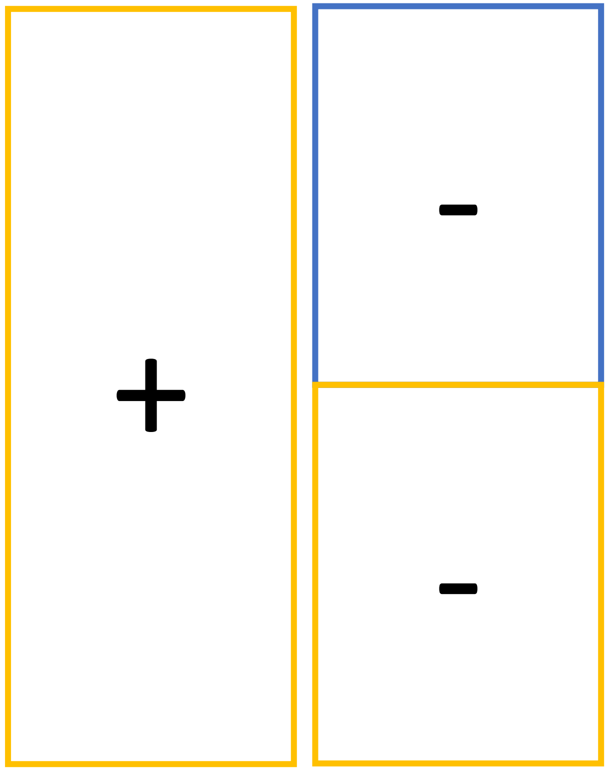
- Solvent
  - Water
- Strong ions (full dissociation)
  - Fixed charges (Na, K, Mg, Cl)
- Weak ions (partial dissociation)
  - Variable charges (HCO3, P)

Isohydric principle for weak acids



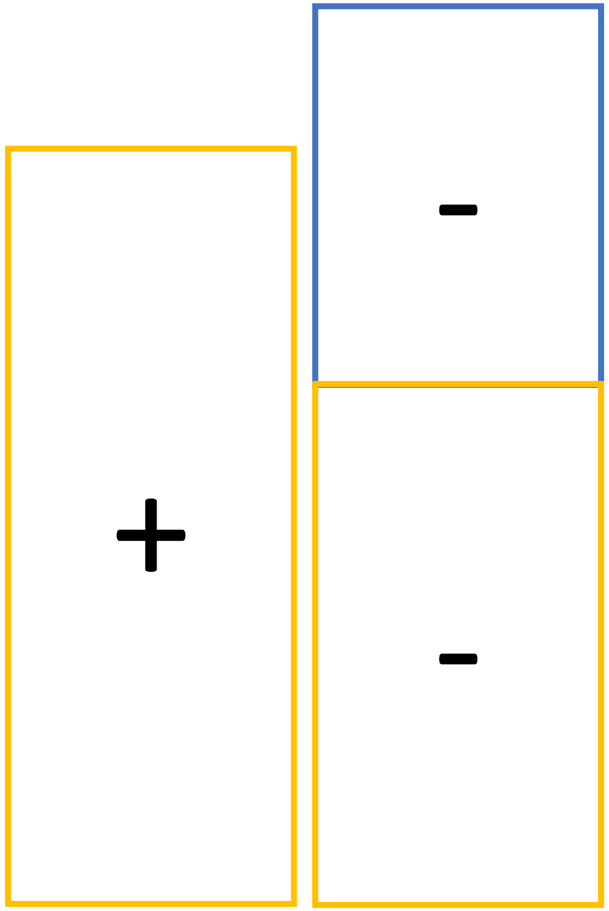
$$\mathrm{p}K_a1 + \log \frac{HCO_3^-}{H_2CO_3} = \mathbf{pH} = \mathrm{p}K_a2 + \log \frac{HPO_4^{2-}}{H_2PO_4^-}$$

Electroneutrality



$$\sum[cations] = \sum[anions]$$

Electroneutrality



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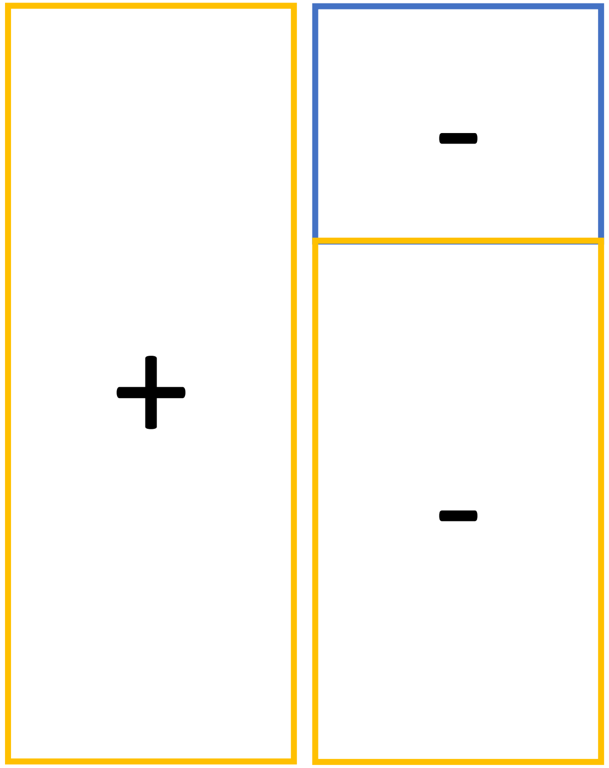
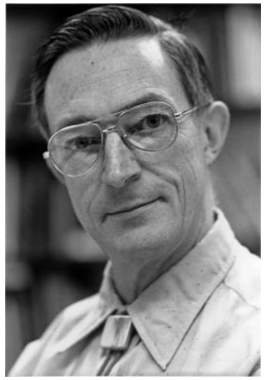
Electroneutrality



$$\sum[cations] = \sum[anions]$$



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Solvent – pure water!

$$H_2O \leftrightarrow OH^- + H^+$$

$\boxed{H^+}$ $\boxed{OH^-}$

$$K_w = [OH^-]\,[H^+]$$

$$\sum[cations] = \sum[anions]$$

$$K_w \; at \; 37° = 2.4 \times 10^{-14}$$

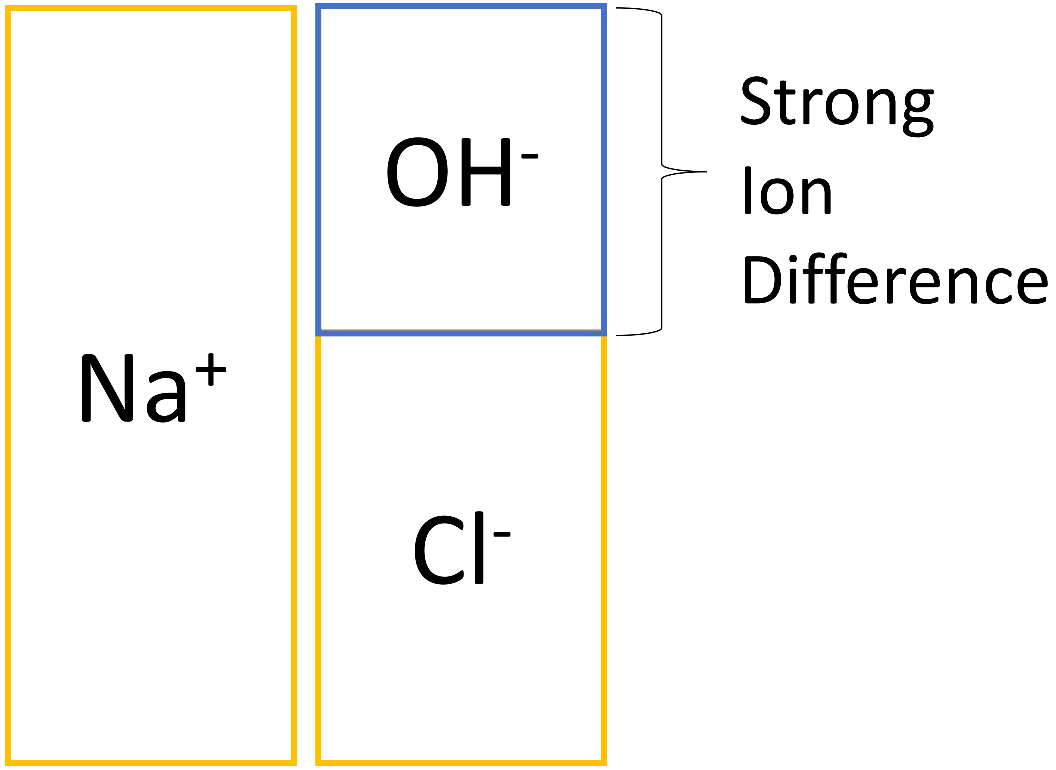
$$[H^+] = 1.55 \times 10^{-7}$$

$$pH = 6.8 \; at \; 37°$$

Strong ions – salt!

Solution with:

- NaOH (Na^+)
- HCl (Cl^-)



$$K_w = [OH^-]\,[H^+]$$

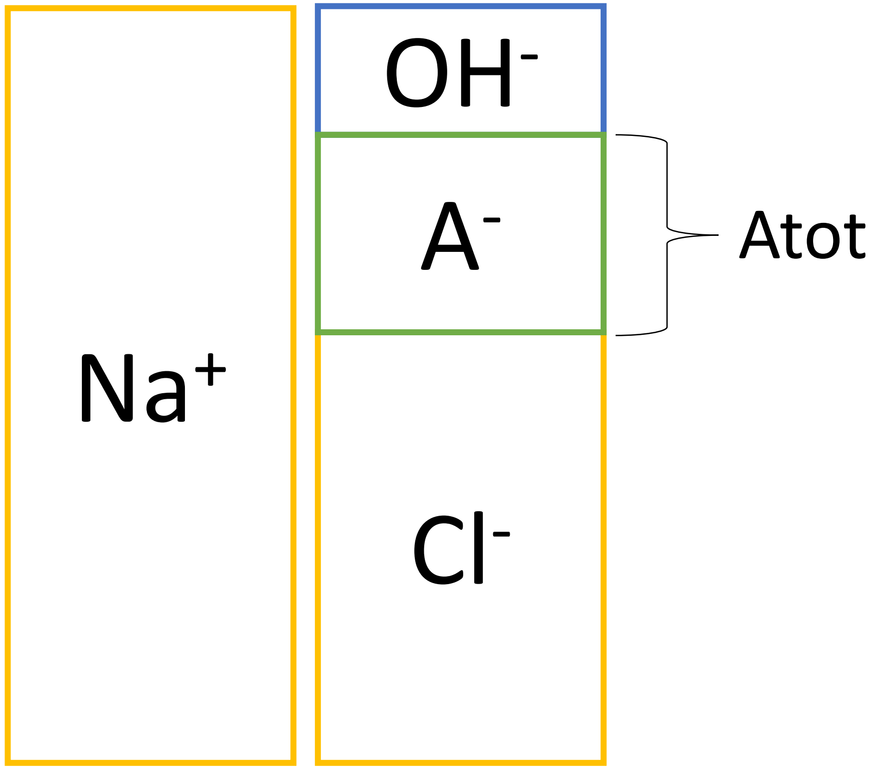
$$pH = 12$$

$$\sum [cations] = \sum [anions]$$

Non-volatile weak ions – buffers!

Solution with:

- Strong ions
- Non-volatile weak acids



$$K_w = [OH^-]\,[H^+]$$

$$pH = 10$$

$$\sum[cations] = \sum[anions]$$

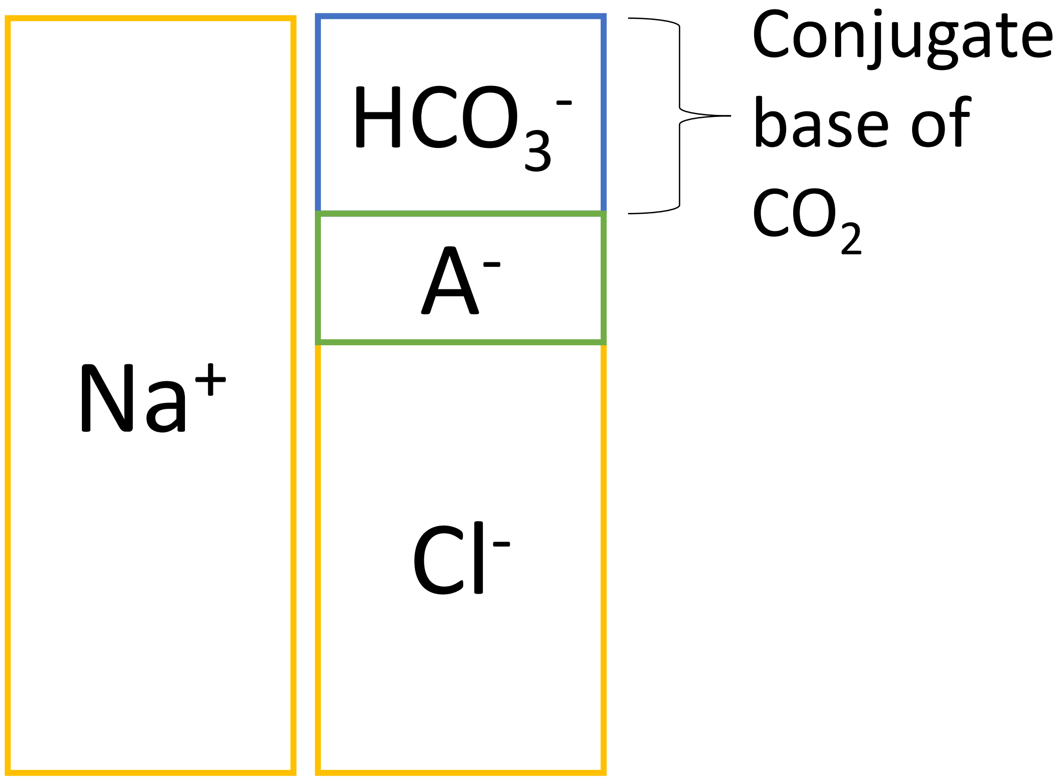
Volatile weak ion – bicarbonate!

Solution with:

- Strong ions
- Non-volatile weak acids
- Volatile weak acids (CO_2)

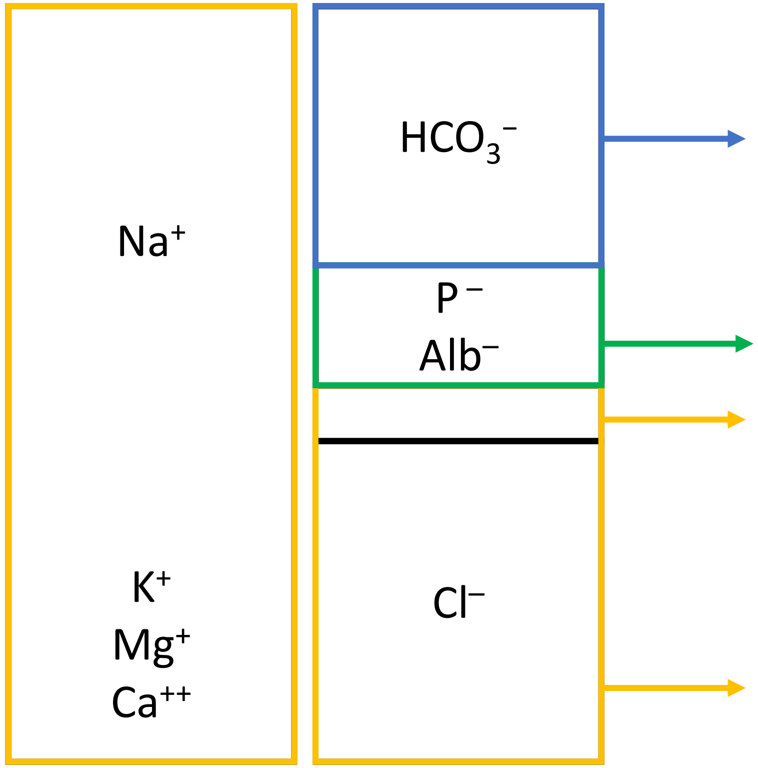
$$K_w = [OH^-]\,[H^+]$$

$$pH = 7.4$$



$$\sum[cations] = \sum[anions]$$

Total solution & unmeasured ions?



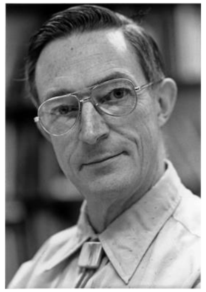
[pCO2] driven hydrolysis

Non-volatile weak acids [A^-]
unmeasured ions [SIG]

$\Big\}$ Anion gap

- Acetoacetic acid, βHB-acid, Sulfate, citrate, gluconate, D-lactate,

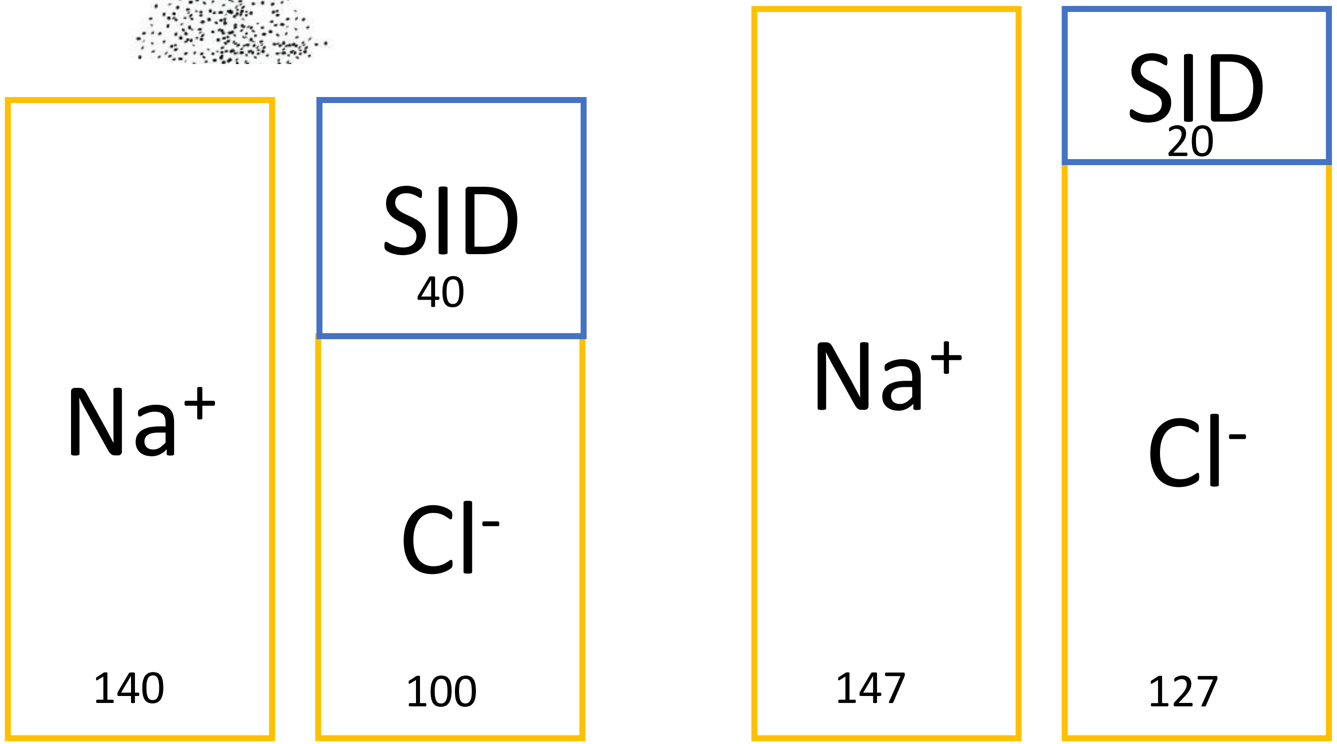
[SID] = measured [cation] – [anion]



pH is a function of water dissociation modified by: strong ions, non-volatile weak acids, and pCO2

Saline acidosis?

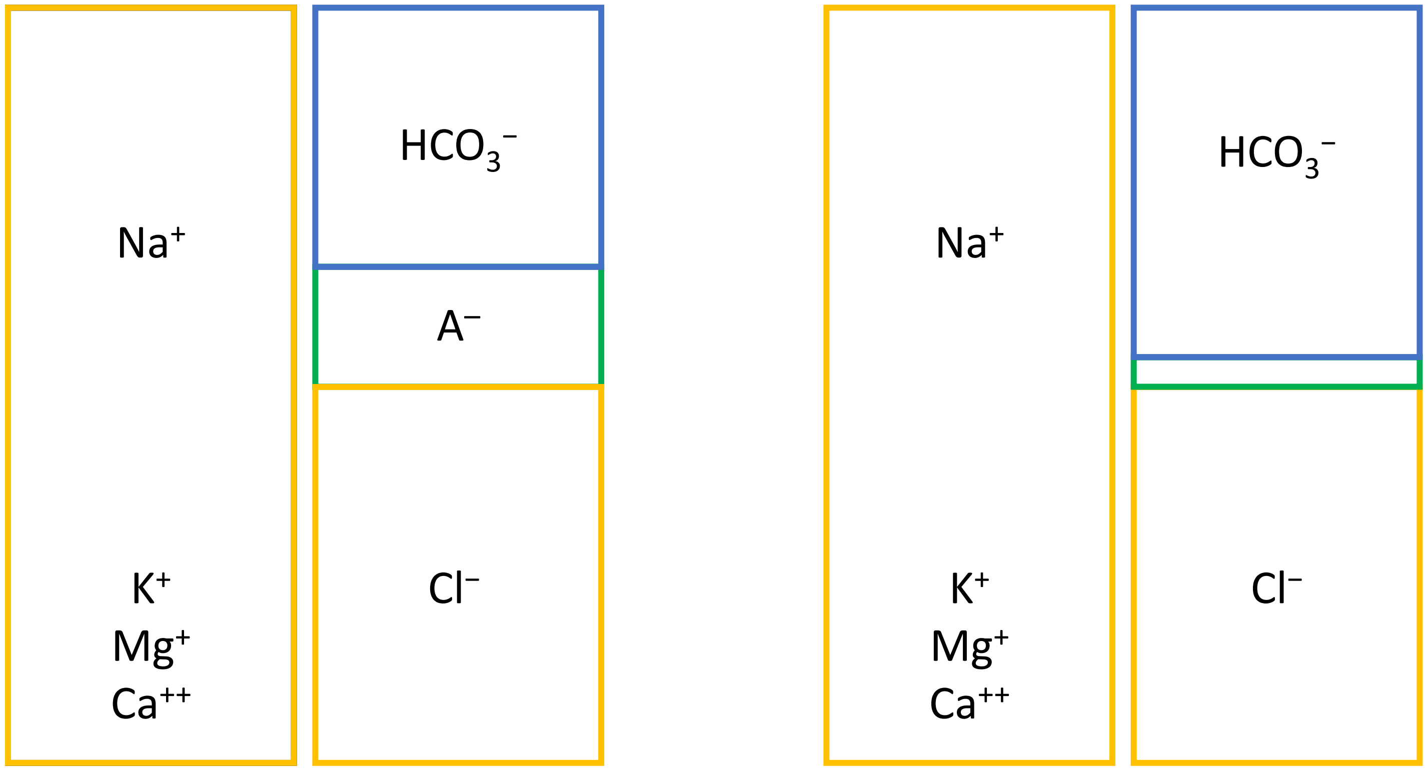
Saline 0.9%
NaCl 154 mmol/l



No change in:
- Atot
- CO2

Change:
- Increase chloride
- Decrease SID
- Decrease pH

Hypoalbuminemia?



No change in:

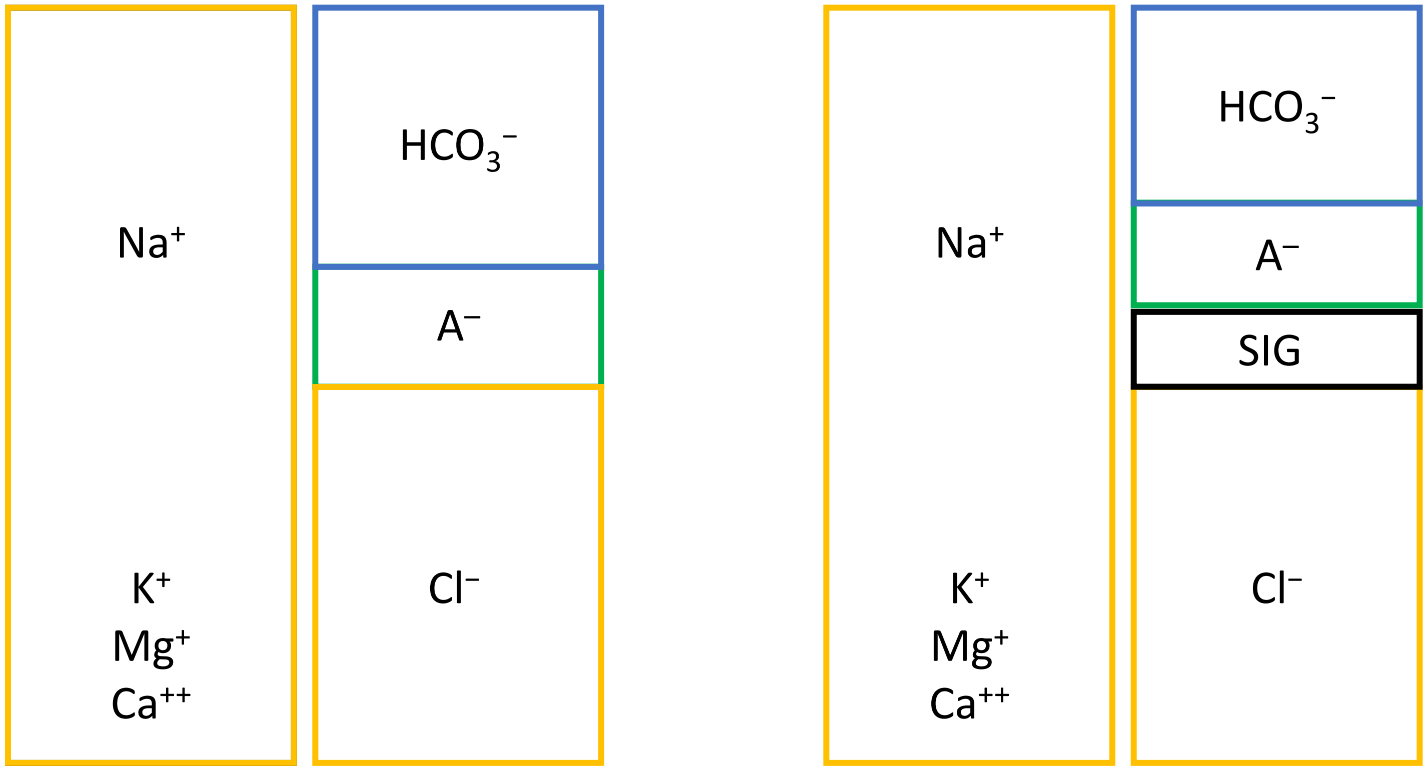
- SID
- CO2

Change:

- Atot
- Increase pH

$$pH = 6.1 + log\frac{HCO_3^-}{\alpha \times pCO_2}$$

Unmeasured ions?



Glycols
Oxoproline
L-lactate
D-lactate
Methanol
Aspirin
Renal failure
Ketoacidosis

$$Strong\ ion\ gap = SID\ - HCO_3^- - A^-$$

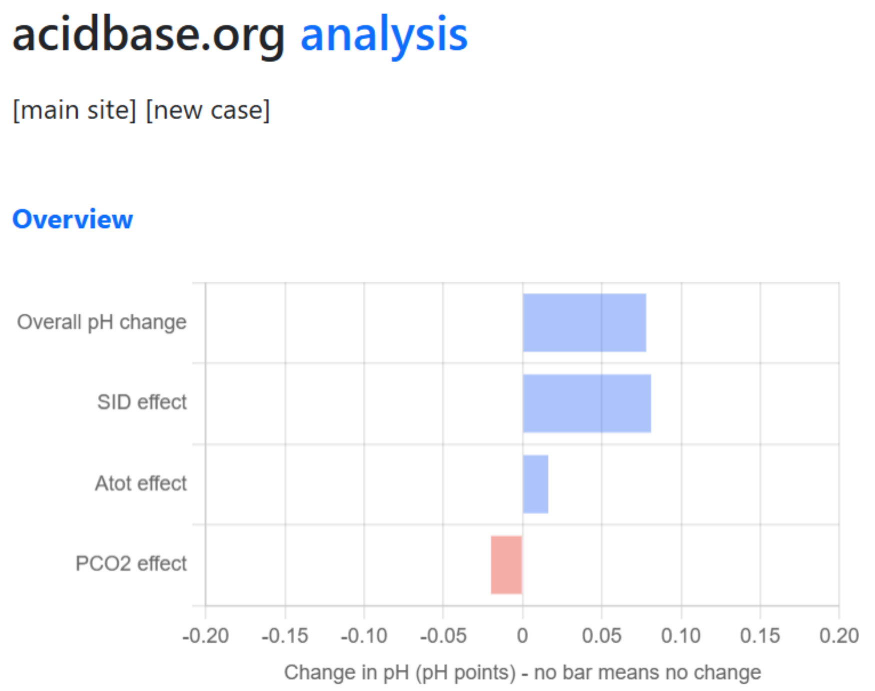
Conclusion

The difference between all methods is how **bicarbonate** is treated!

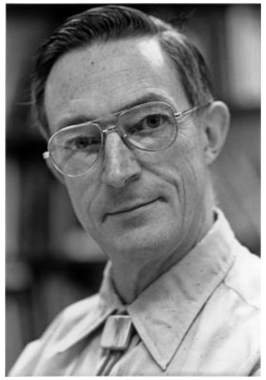
Electrical neutrality and three independent variables

- Strong ion difference
- Non-volatile weak acids (Atot)
- Carbon dioxide

How do I use this in practice?



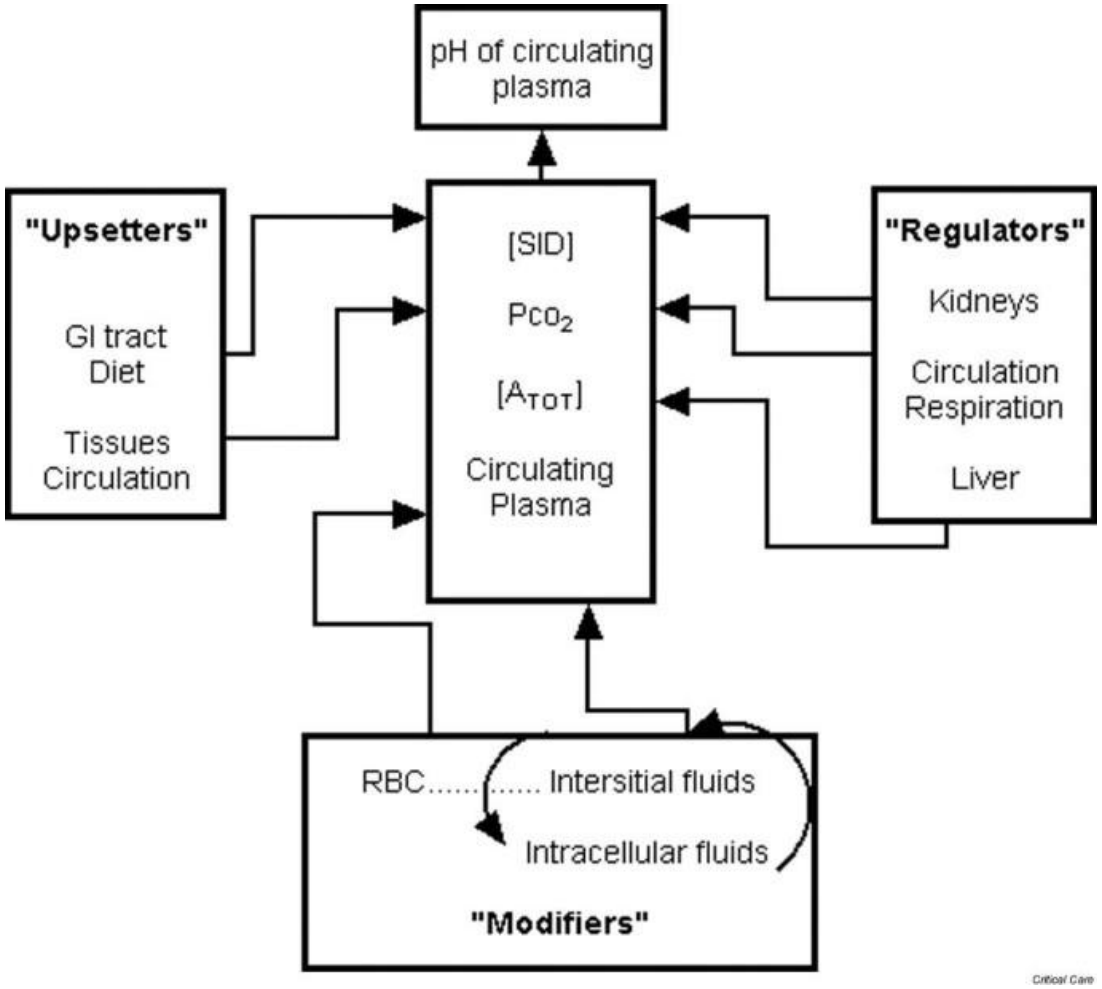
Can you actually calculate with it?

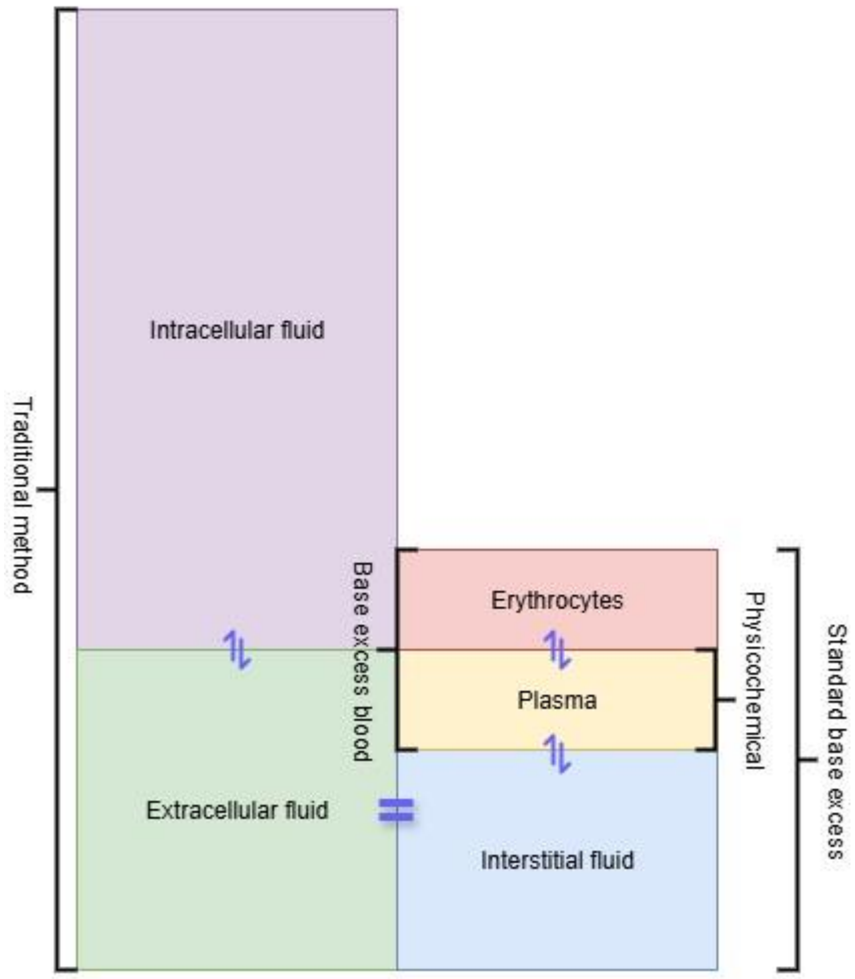


$$pH = 6.1 + \log_{10} \frac{[SID] - [A^-] - [SIG]}{0.03\, pCO_2}$$

QUESTIONS?

Physicochemical approach – an inconvenient truth?





The bottom line

	Traditional	Base excess (ecf)	Stewart
Type			
Complexity level			
Markers			
Satisfactory pH mechanism			
pH culprit identification			
Compartments			
Intracellular buffers			
Advantages			
Disadvantages			

Brønsted–Lowry

Acid is a proton donor

Base is a proton acceptor

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Concerned with equilibrium of pairs