



pH and buffers

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K_w

$$K_{eq} (55.5 \text{ M}) = [\text{H}^{\oplus}] [\text{OH}^{\ominus}]$$

$$K_w = [\text{H}^{\oplus}] [\text{OH}^{\ominus}] = 1.0 \times 10^{-14} \text{ M}^2$$

- K_w is called the ion product for water.

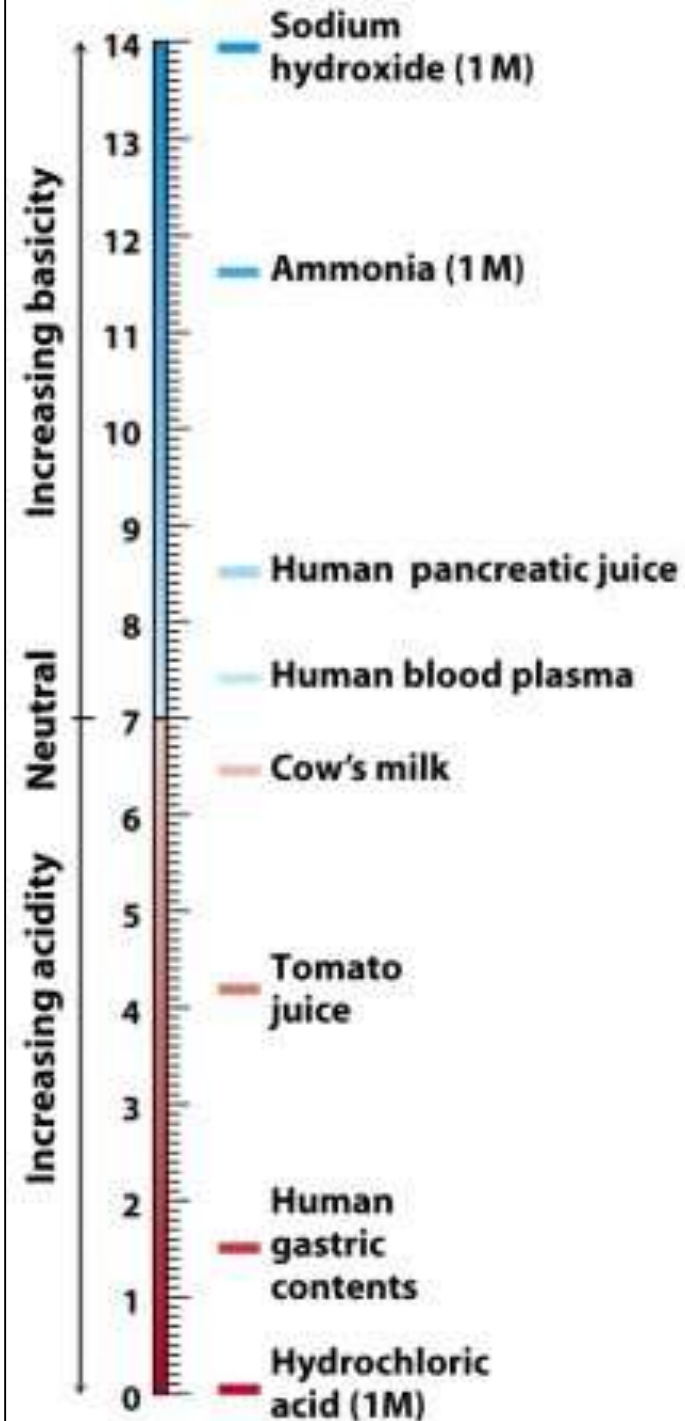
TABLE 2.3 Relation of $[\text{H}^{\oplus}]$ and $[\text{OH}^{\ominus}]$ to pH

pH	$[\text{H}^{\oplus}]$ (M)	$[\text{OH}^{\ominus}]$ (M)
0	1	10^{-14}
1	10^{-1}	10^{-13}
2	10^{-2}	10^{-12}
3	10^{-3}	10^{-11}
4	10^{-4}	10^{-10}
5	10^{-5}	10^{-9}
6	10^{-6}	10^{-8}
7	10^{-7}	10^{-7}
8	10^{-8}	10^{-6}
9	10^{-9}	10^{-5}
10	10^{-10}	10^{-4}
11	10^{-11}	10^{-3}
12	10^{-12}	10^{-2}
13	10^{-13}	10^{-1}



What is pH?

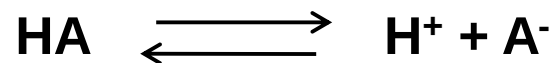
$$\text{pH} = \log_{10}(1/[\text{H}^+]) = -\log_{10}[\text{H}^+]$$





Example 1:

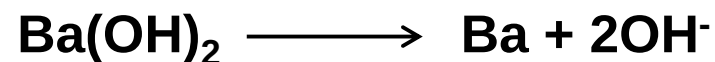
Find the K_a of a 0.04 M weak acid HA whose $[H^+]$ is 1×10^{-4} ?



$$K_a = [A^-] [H^+] / [HA] = [H^+]^2 / [HA] = 10^{-4} \times 10^{-4} / 0.04 = 2.5 \times 10^{-7}$$

Example 2:

What is the $[H^+]$ of a 0.05 M $Ba(OH)_2$?



$$[OH^-] = 2 \times 0.05 = 0.10 \text{ M} = 1 \times 10^{-1}$$

$$[H^+] = 1 \times 10^{-13}$$

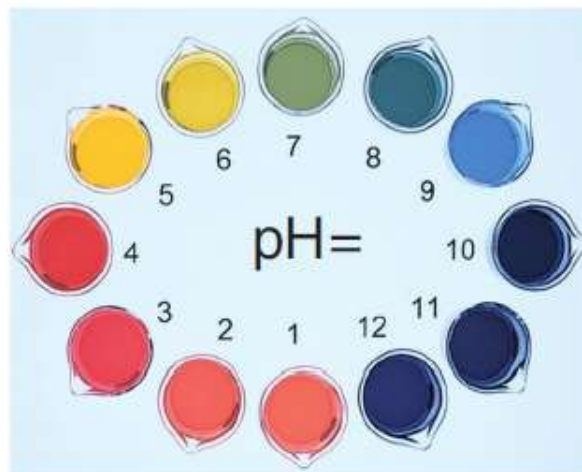


Exercises

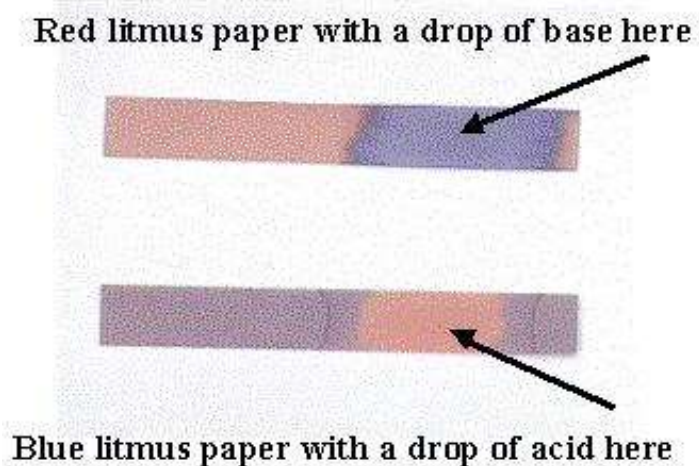
- What is the pH of
 - 0.01 M HCl?
 - 0.01 M H₂SO₄?
 - 0.01 M NaOH?
 - 1×10^{-11} M HCl? (this is a tricky one)
 - 0.1 M of acetic acid (CH₃COOH)? Remember Ka

Determination of pH

- Acid-base indicator
 - Litmus paper (least accurate)
 - Universal indicator
- An electronic pH meter (most accurate)



(a)



(b)



Henderson-Hasselbalch equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

pH	=	acidity of a buffer solution
pKa	=	negative logarithm of Ka
Ka	=	acid disassociation constant
[HA]	=	concentration of an acid
[A-]	=	concentration of conjugate base

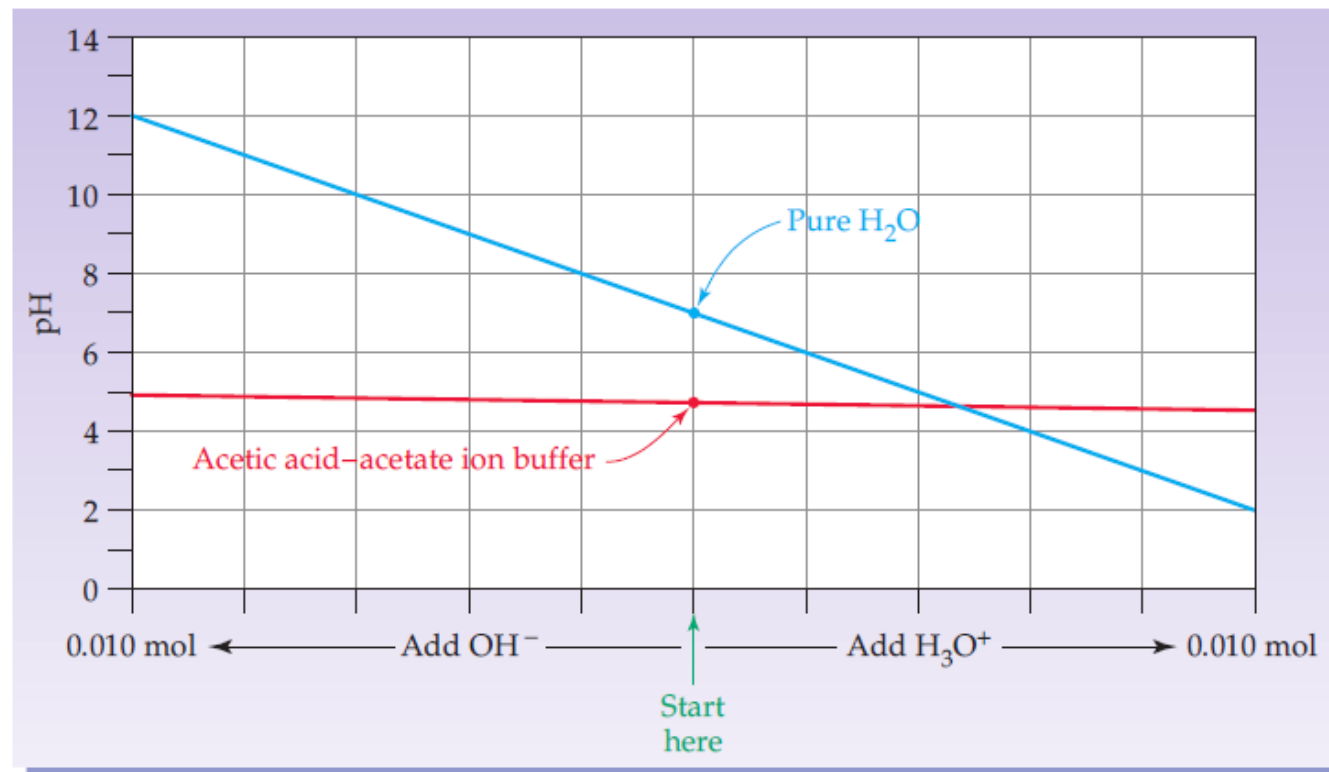
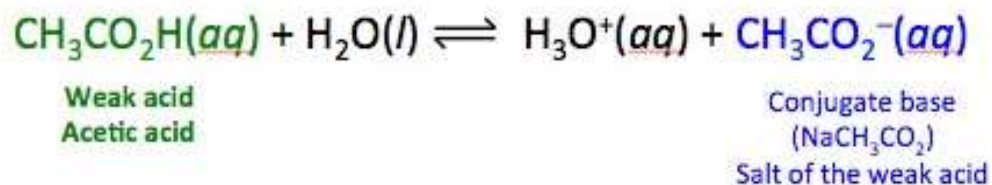
pKa is the pH where 50% of an acid is dissociated into its conjugate base.

pKa is the pH where the concentration of the acid is equal to that of the conjugate base.



A comparison of the change in pH (water vs. acetic acid)

- 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of an acetate solution composed of 0.10 M acetic acid and 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.





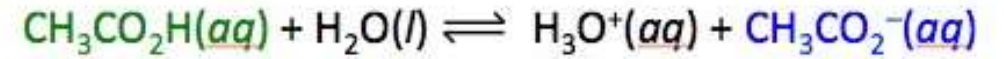
What is a buffer?

- Buffers are solutions that resist changes in pH by changing reaction equilibrium.
- They are usually composed of mixtures of a weak acid and an equal concentration of its conjugate base (*salt*).

Acid	Conjugate base
CH_3COOH	CH_3COONa (NaCH_3COO)
H_3PO_4	NaH_2PO_4
H_2PO_4^- (or NaH_2PO_4)	Na_2HPO_4
H_2CO_3	NaHCO_3



Titration curve of buffer

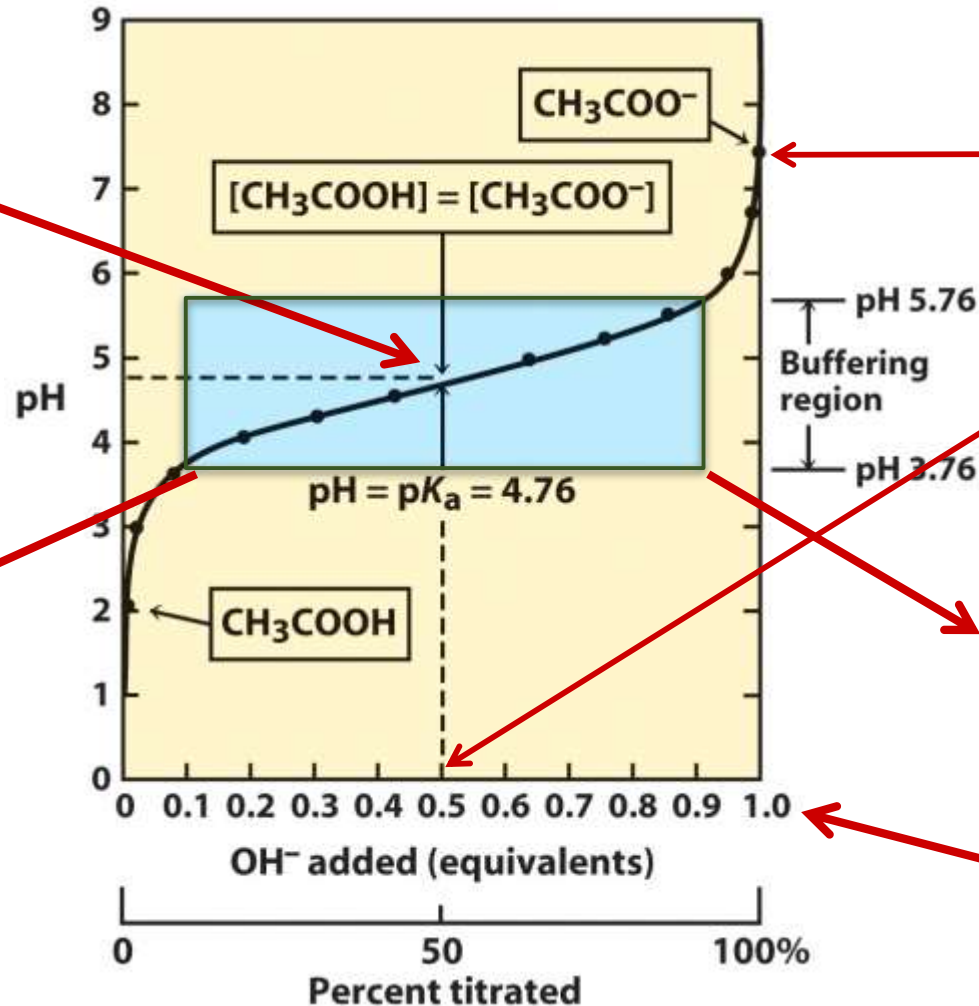


Weak acid
Acetic acid

Conjugate base
(NaCH_3CO_2)
Salt of the weak acid

What is the midpoint (inflection point)?

What is the ratio of the conjugate base:acid at the different points?



Equivalence point

Half equivalence point

Buffering range ($\text{pK}_a \pm 1$)

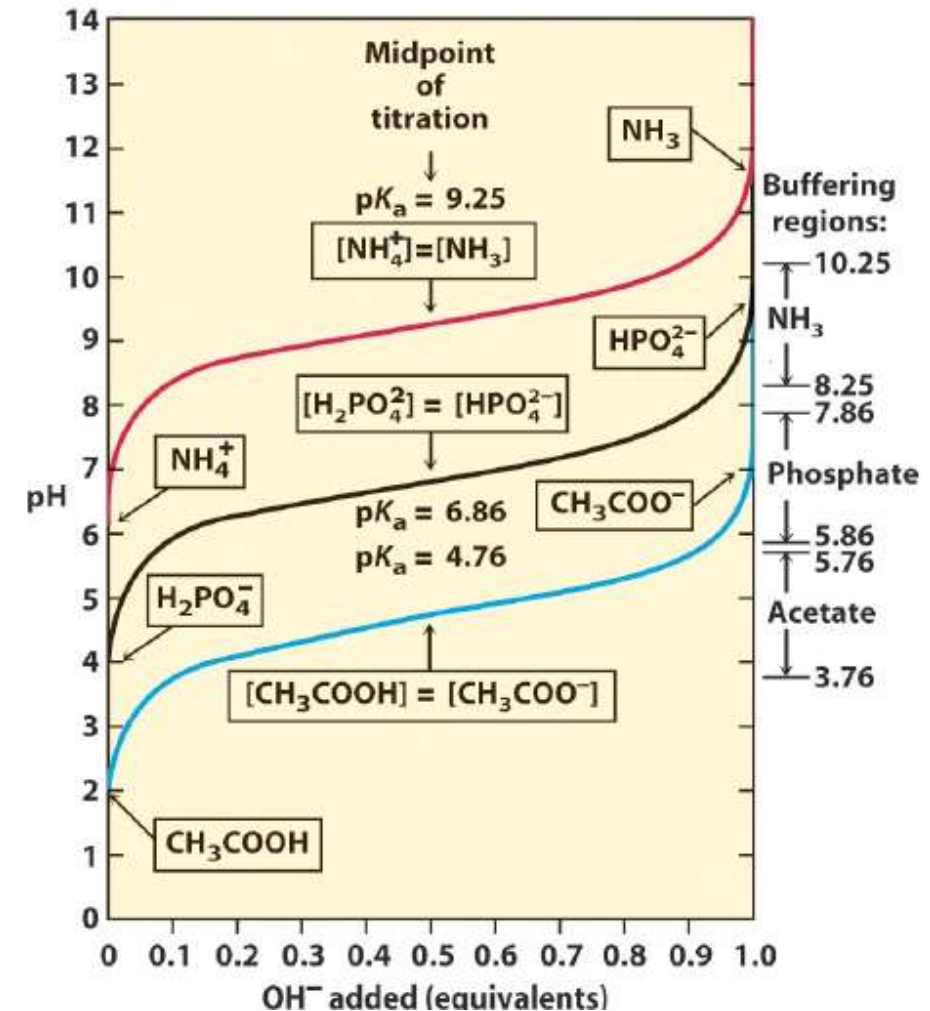
Note the equivalents of the added base (or acid)



How do we make/choose a buffer?

- A buffer is made by combining weak acid/base and its salt.
- The buffering capacity of a buffer to function depends on:
 - Buffer concentration
 - Buffering range
 - pK_a of the buffer
 - The desired pH

Note: increasing the concentration does not change the buffering range but it increases buffering capacity or strength.





Exercise

- A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pKa of acetic acid is 4.8. Hence, the pH of the solution is given by

$$\text{pH} = 4.8 + \log(0.2/0.1) = 4.8 + \log 2.0 = 4.8 + 0.3 = 5.1$$

- Similarly, the pKa of an acid can be (

**Since you are smart, you
can estimate it.
No calculator is needed.**



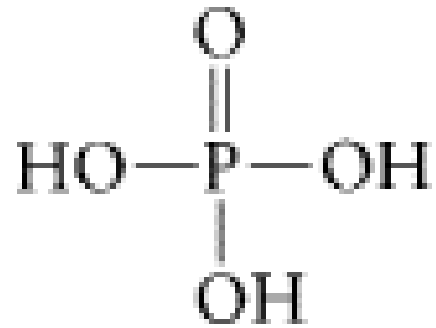
Base 10 Logarithms

$\text{Log}_{10}(0.01)=-2$	since $10^{-2}=1/100$
$\text{Log}_{10}(0.1)=-1$	since $10^{-1}=1/10$
$\text{Log}_{10}(1)=0$	since $10^0=1$
$\text{Log}_{10}(10)=1$	since $10^1=10$
$\text{Log}_{10}(100)=2$	since $10^2=100$
$\text{Log}_{10}(1000)=3$	since $10^3=1000$

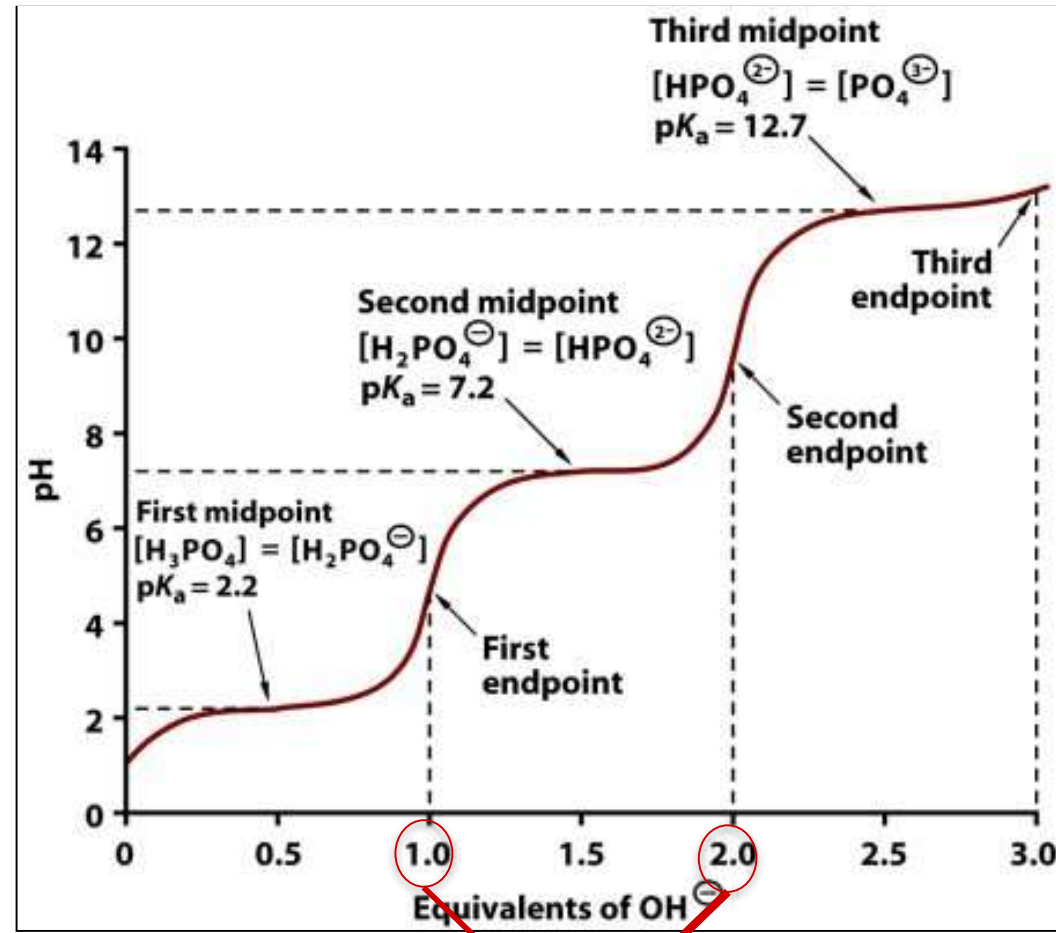
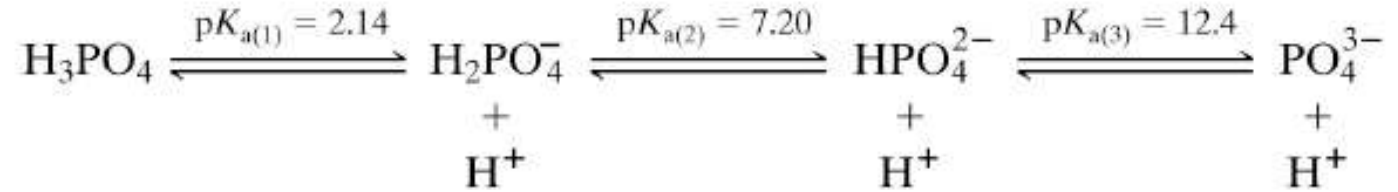


Exercise

1. Predict then calculate the pH of a buffer containing
 - 0.1M HF and 0.12M NaF? ($K_a = 3.5 \times 10^{-4}$)
 - 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?
2. What is the pH of a lactate buffer that contains 75% lactic acid and 25% lactate? ($pK_a = 3.86$)
3. What is the concentration of 5 ml of acetic acid that can be titrated completely by 44.5 ml of 0.1 M NaOH?
 - The number of equivalents of OH^- required for complete neutralization is equal to the number of equivalents of hydrogen ion present as H^+ and HA.



Titration curve of
phosphate buffer



Note values



Exercises

1. What is the pKa of a dihydrogen phosphate buffer when a pH of 7.2 is obtained when 100 ml of 0.1 M NaH_2PO_4 is mixed with 100 ml of 0.3 M Na_2HPO_4 ?
2. A solution was prepared by dissolving 0.02 moles of acetic acid (pKa = 4.8) in water to give 1 liter of solution.
 - What is the pH?
 - To this solution, 0.008 moles NaOH were added. What is the new pH? (ignore changes in volume).

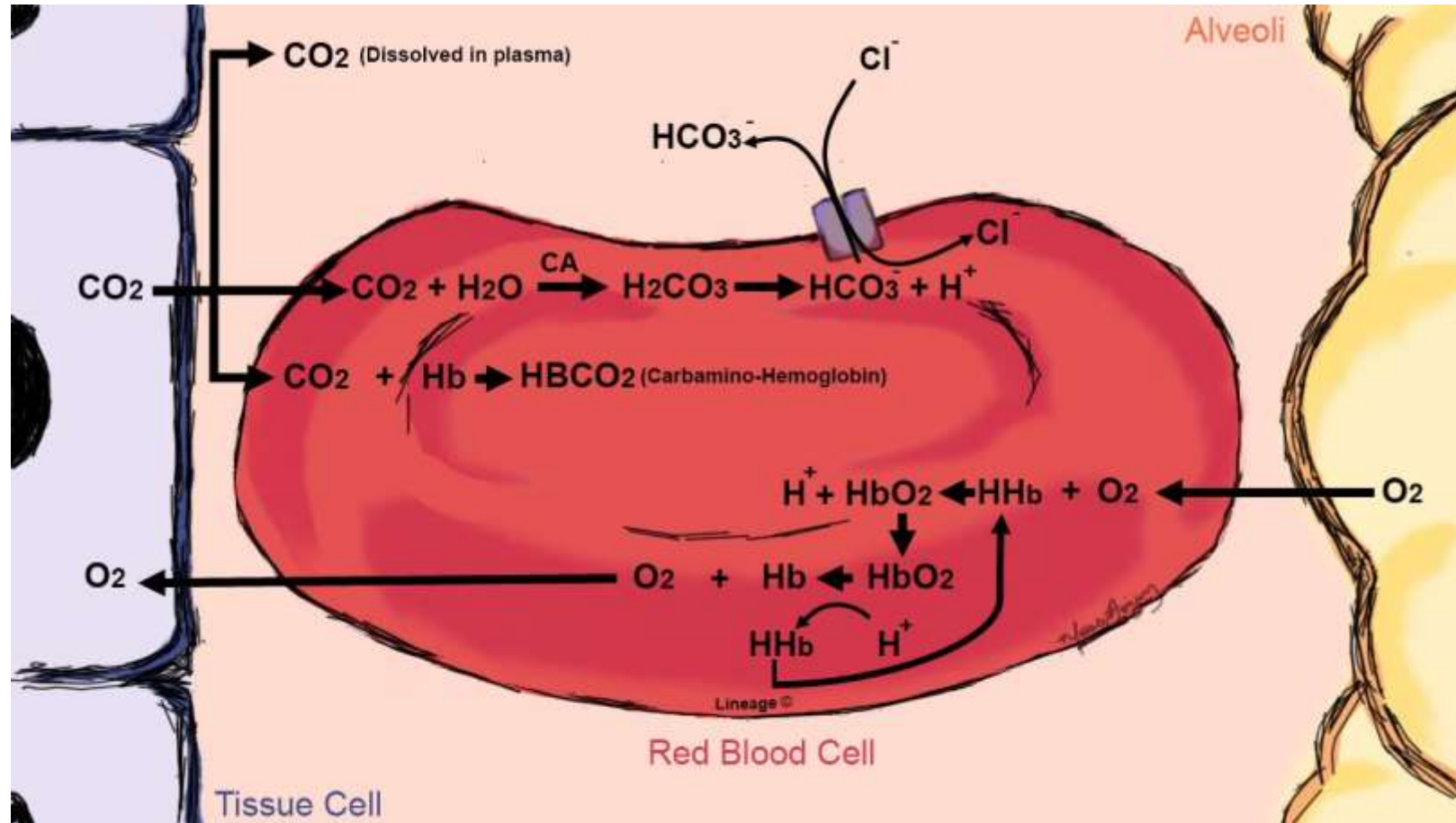


Biological buffers in human body

- Carbonic acid-bicarbonate system (blood)
- Dihydrogen phosphate-monohydrogen phosphate system (intracellular)
 - ATP, glucose-6-phosphate, bisphosphoglycerate (RBC)
- Proteins (why?)
 - Hemoglobin in blood
 - Other proteins in blood and cells

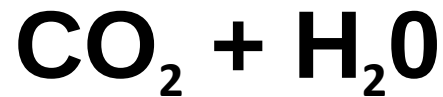
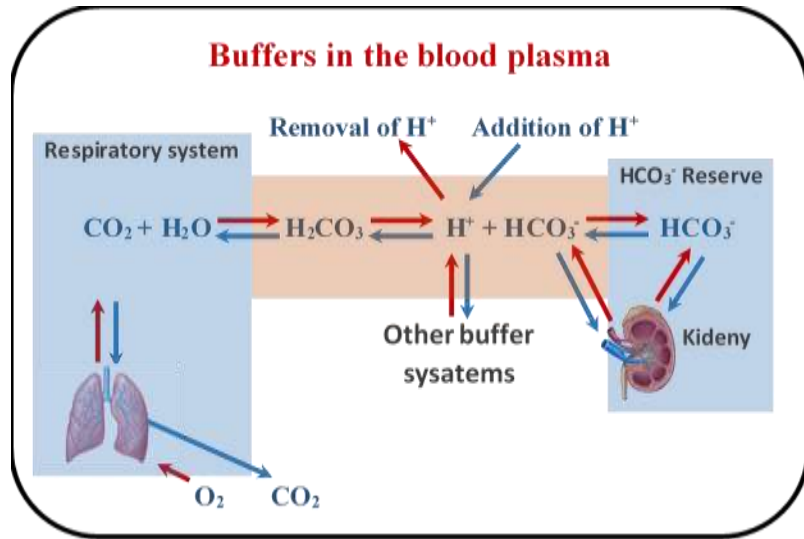


Bicarbonate buffer in the human system

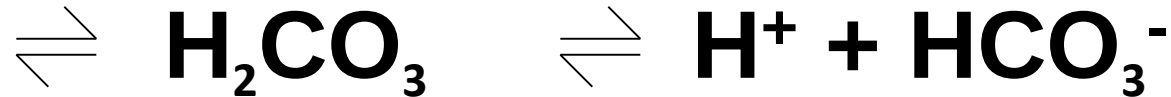




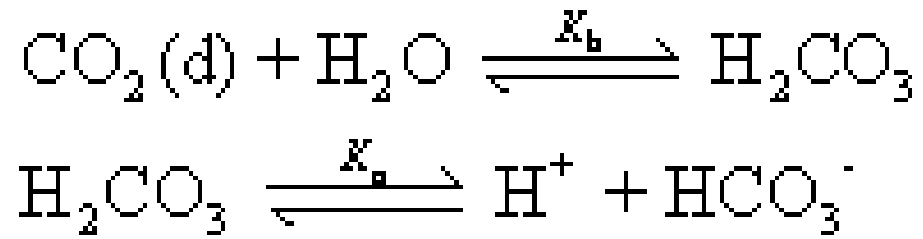
Bicarbonate buffer



Lungs
(within minutes)



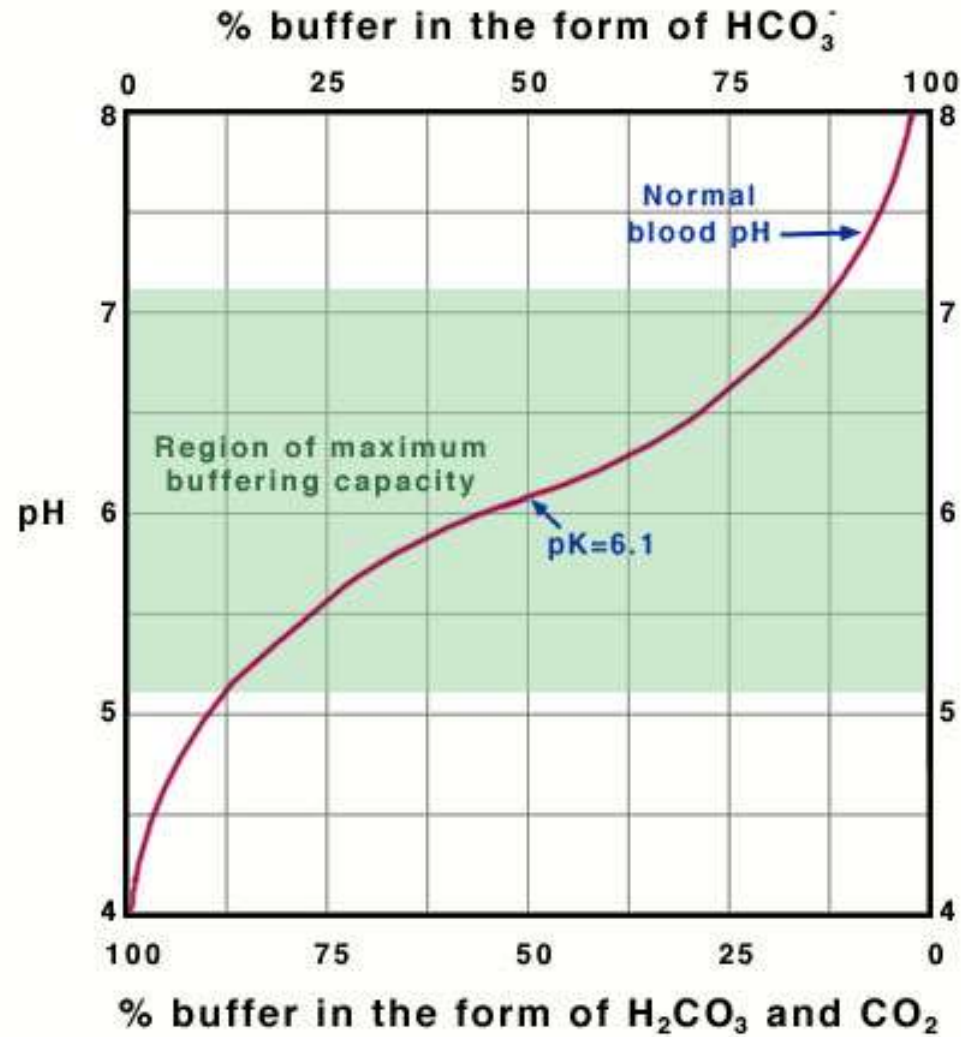
Excretion via kidneys (hours to days)



Blood (instantaneously)

Titration curve of bicarbonate buffer

Note pKa





Why is this buffer effective?

- Even though the normal blood pH of 7.4 is outside the optimal buffering range of the bicarbonate buffer, which is 6.1, this buffer pair is important due to two properties:
 - Bicarbonate is present in a relatively high concentration in the ECF (24mmol/L).
 - The components of the buffer system are effectively under physiological control: the CO_2 by the lungs, and the bicarbonate by the kidneys.
 - It is an open system (not a closed system like in laboratory).
 - An open system is a system that continuously interacts with its environment.



Acidosis and alkalosis

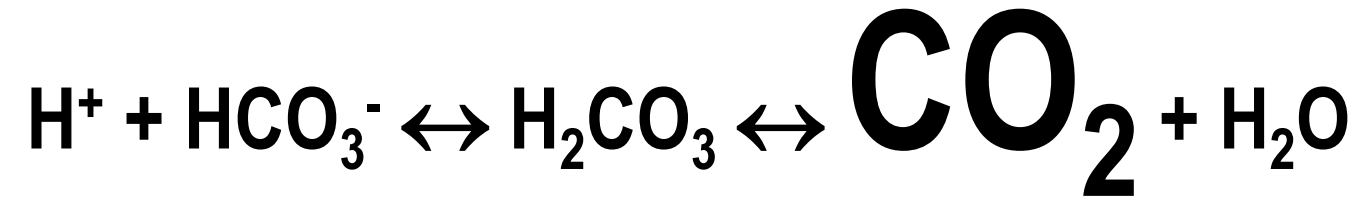
- Both pathological conditions can be either metabolic or respiratory.
- Acidosis ($\text{pH} < 7.35$)
 - Metabolic: production of ketone bodies (starvation and diabetes)
 - Respiratory: pulmonary (asthma; emphysema)
- Alkalosis ($\text{pH} > 7.45$)
 - Metabolic: excessive administration of salts
 - Respiratory: hyperventilation (anxiety)

Normal ABG Figures	
PH	7.35-7.45
PO ₂	80-100
PCO ₂	35-45
HC0 ₃	22-28

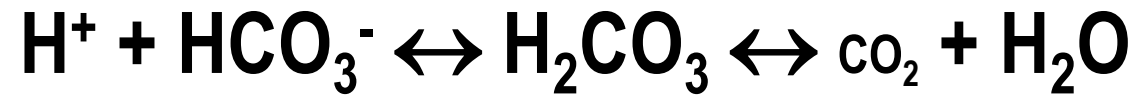


Respiratory conditions

Respiratory Acidosis



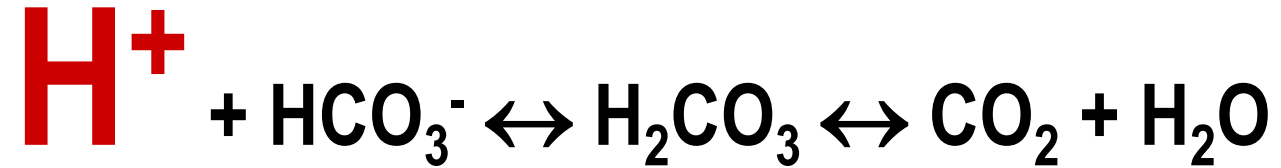
Respiratory Alkalosis





Metabolic conditions

Metabolic Acidosis

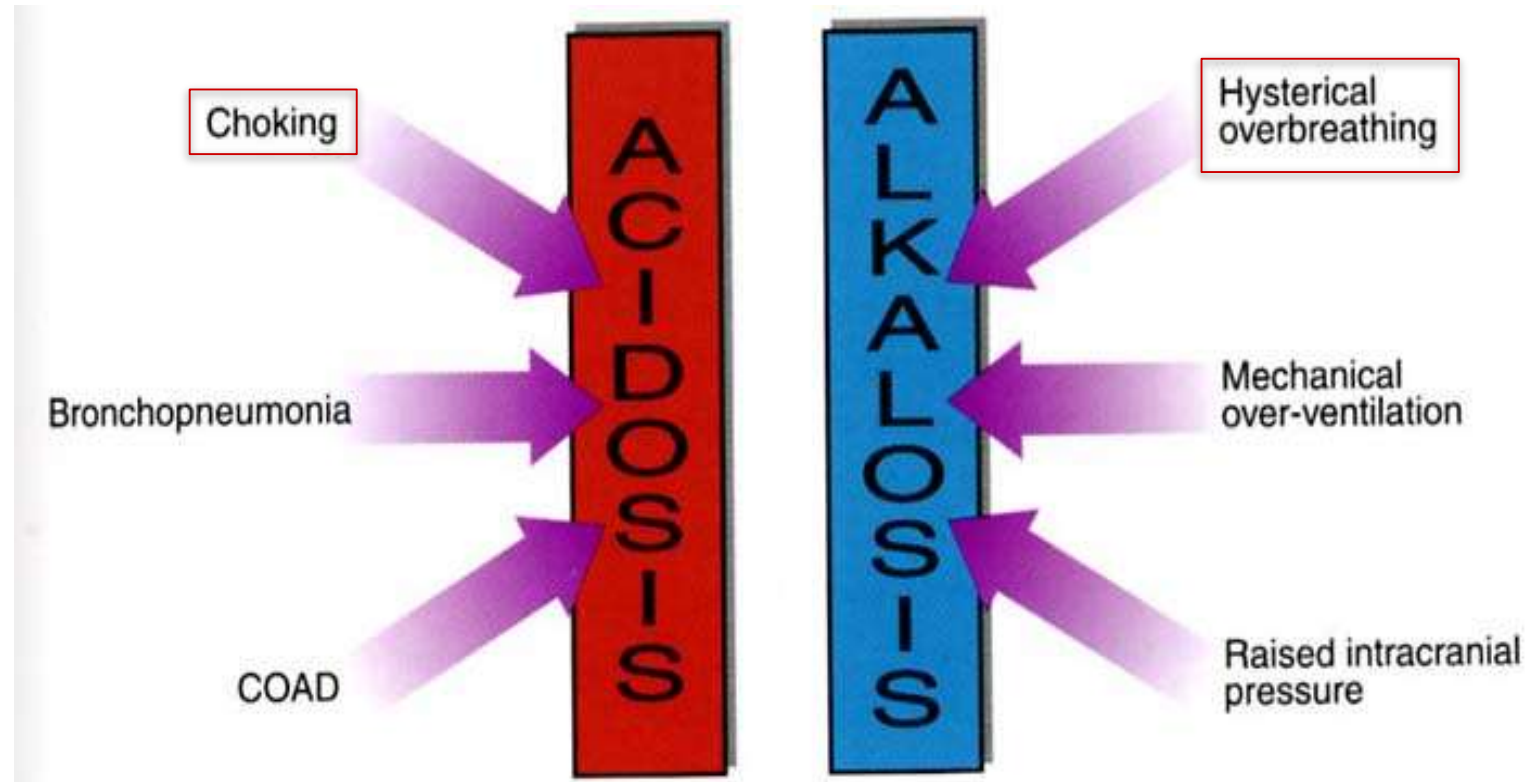


Metabolic Alkalosis

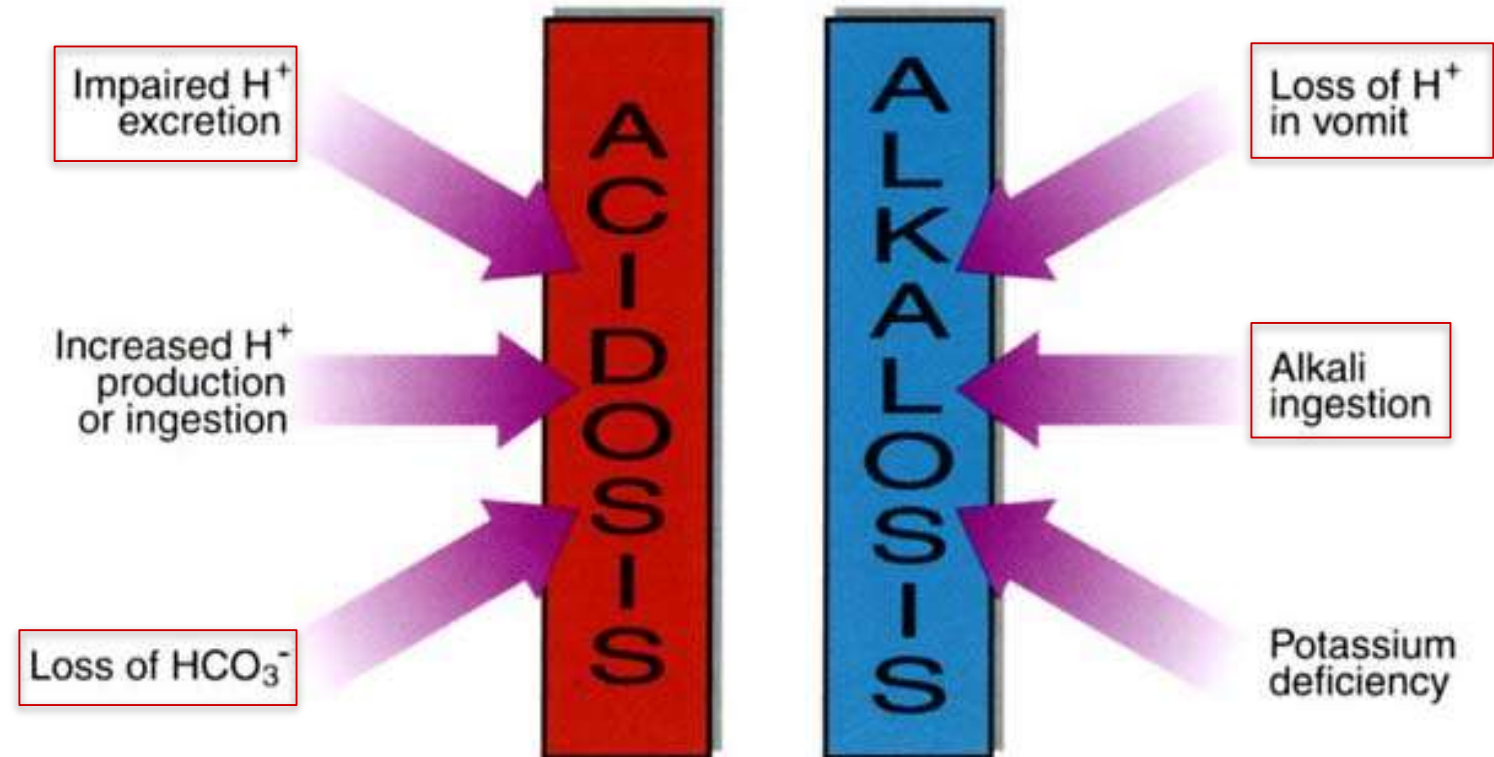




Causes of respiratory acid-base disorders



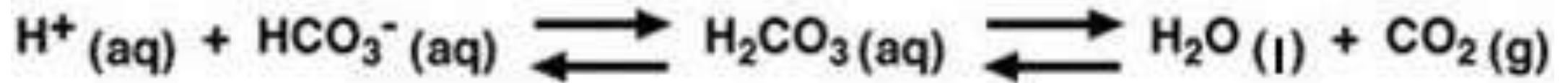
Causes of metabolic acid-base disorders

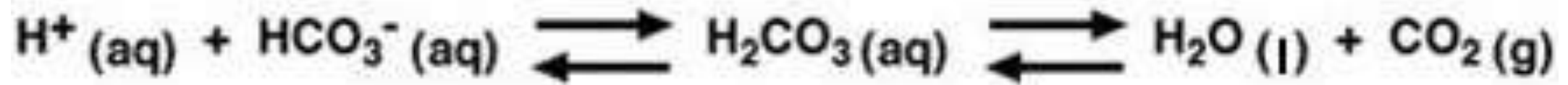




Compensation

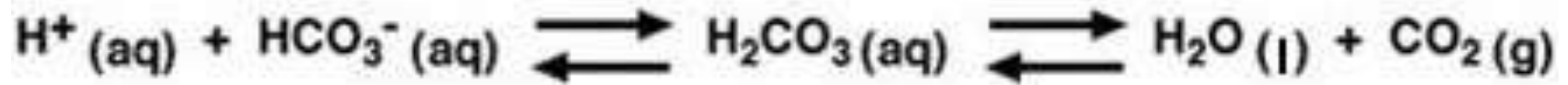
- **Compensation**: A change in HCO_3^- or pCO_2 as a result of the primary event in order to return the pH to normal levels.
- If the underlying problem is metabolic, hyperventilation or hypoventilation alters pCO_2 ; it is called **respiratory compensation**.
- If the problem is respiratory, renal mechanisms drives **metabolic compensation** via changing $[\text{HCO}_3^-]$.
- Complete compensation if brought back within normal limits
- Partial compensation if the pH is still outside norms.





FULL
COMPENSATION

	pH	pCO ₂	HCO ₃ ⁻
Resp. acidosis	Normal But < 7.40	↑	↑
Resp. alkalosis	Normal but > 7.40	↓	↓
Met. Acidosis	Normal but < 7.40	↓	↓
Met. alkalosis	Normal but > 7.40	↑	↑



PARTIAL
COMPENSATION

	pH	pCO ₂	HCO ₃ ⁻
Res.Acidosis	↓	↑	↑
Res.Alkalosis	↑	↓	↓
Met. Acidosis	↓	↓	↓
Met.Alkalosis	↑	↑	↑



Example 1

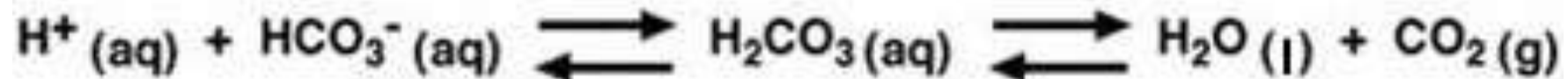
- Mrs. X is admitted with severe attack of asthma. Her arterial blood gas result is as follows:

- pH : 7.22
- $p\text{CO}_2$: 55
- HCO_3^- : 25

- pH is low – acidosis
- $p\text{CO}_2$ is high – in the opposite direction of the pH.
- HCO_3^- is Normal

- Respiratory Acidosis

Normal ABG Figures	
PH	7.35-7.45
PO2	80-100
PCO2	35-45
HC03	22-28





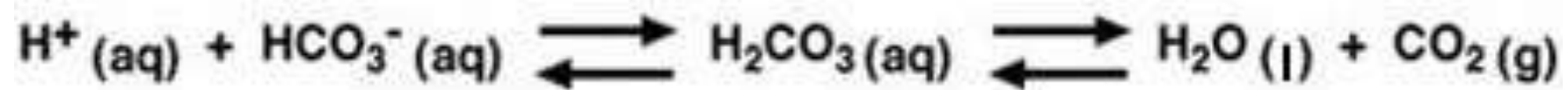
Example 2

- Mr. D is admitted with recurring bowel obstruction and has been experiencing continuous vomiting for the last several hours. His ABG is:

- pH: 7.5
- pCO₂: 42
- HCO₃⁻: 33

Normal ABG Figures	
PH	7.35-7.45
PO2	80-100
PCO2	35-45
HC03	22-28

- Metabolic alkalosis

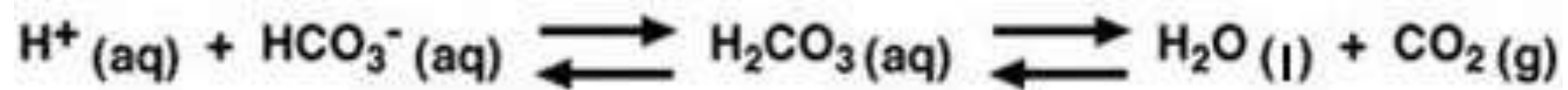




Example 3

- Mrs. H is a kidney dialysis patient who has missed his last 2 appointments at the dialysis center. His ABG results:
 - pH: 7.32
 - pCO₂: 32
 - HCO₃⁻: 18
- Partially compensated metabolic Acidosis

Normal ABG Figures	
PH	7.35-7.45
PO2	80-100
PCO2	35-45
HC03	22-28

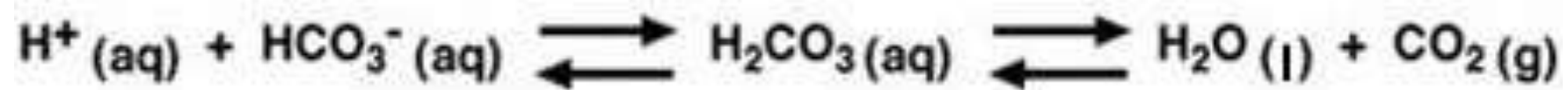


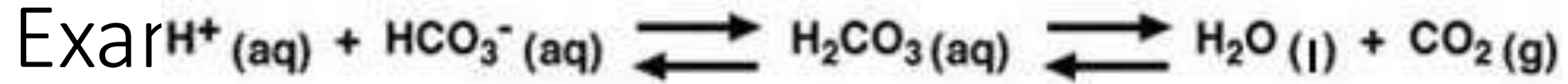


Example 4

- Mr. K with Chronic obstructive pulmonary disease (COPD). His ABG is:
 - pH: 7.35
 - pCO₂: 48
 - HCO₃⁻:30
- Fully compensated Respiratory Acidosis

Normal ABG Figures	
PH	7.35-7.45
PO2	80-100
PCO2	35-45
HC03	22-28





- Mr. S is a 53-year-old man presented to ED with the following ABG.

- pH: 7.51
- pCO_2 : 50
- HCO_3^- : 40

- Metabolic alkalosis with partial compensation

Normal ABG Figures	
PH	7.35-7.45
PO2	80-100
PCO2	35-45
HC03	22-28



Practice ABG's

1. pH 7.48	PaCO ₂ 32	HCO ₃ ⁻ 24
2. pH 7.32	PaCO ₂ 48	HCO ₃ ⁻ 25
3. pH 7.30	PaCO ₂ 40	HCO ₃ ⁻ 18
4. pH 7.38	PaCO ₂ 48	HCO ₃ ⁻ 31
5. pH 7.49	PaCO ₂ 40	HCO ₃ ⁻ 30
6. pH 7.35	PaCO ₂ 48	HCO ₃ ⁻ 27
7. pH 7.45	PaCO ₂ 47	HCO ₃ ⁻ 29
8. pH 7.31	PaCO ₂ 38	HCO ₃ ⁻ 15
9. pH 7.30	PaCO ₂ 50	HCO ₃ ⁻ 24
10. pH 7.48	PaCO ₂ 40	HCO ₃ ⁻ 30

Normal ABG Figures

PH	7.35-7.45
PO2	80-100
PCO2	35-45
HC03	22-28



Answers to Practice ABG's

1. Respiratory alkalosis
2. Respiratory acidosis
3. Metabolic acidosis
4. Compensated Respiratory acidosis
5. Metabolic alkalosis
6. Respiratory acidosis
7. Compensated Metabolic alkalosis
8. Metabolic acidosis
9. Respiratory acidosis
10. Metabolic alkalosis

