CHEMICAL EQUILIBRIUM
EQUILIBRIUM CONSTANT
LE CHÂTELIER´S PRINCIPLE

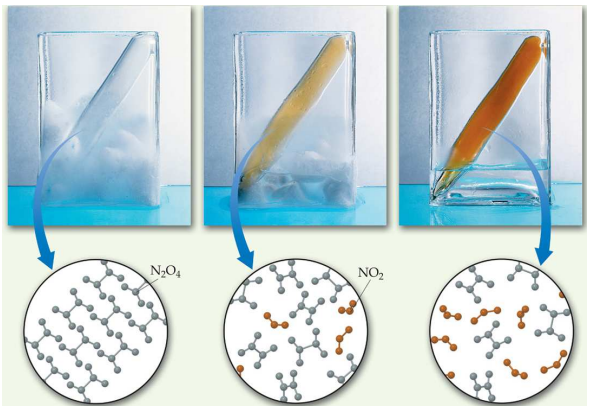
(Zuzana Országhová)

The Concept of Equilibrium

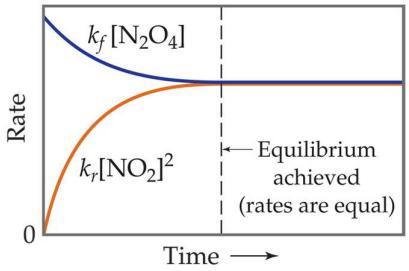
reactant / product: $N_2O_4(g)$ ⇌ $2\,NO_2(g)$: product / reactant

forward →

reverse ←



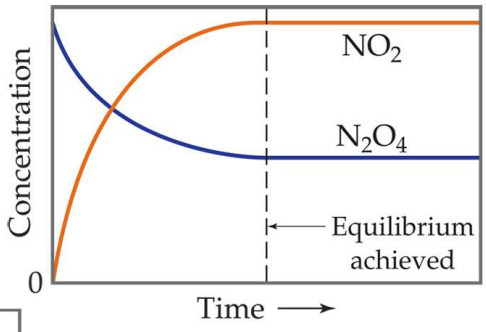
The Concept of Equilibrium

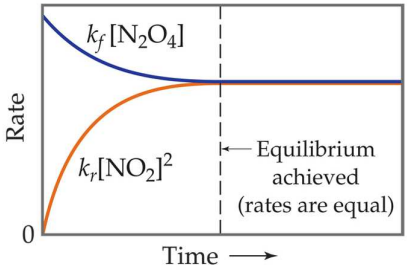


- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding at the same rate.

The System at Equilibrium

Once equilibrium is achieved, the amount of each reactant and product remains constant.





Depicting Equilibrium

In a system at equilibrium, both the forward and reverse reactions are being carried out;

as a result, we write its equation with a double arrow

$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

The Equlibrium Constant

$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$

- **Forward reaction:**
  $N_2O_4\,(g) \longrightarrow 2\,NO_2\,(g)$
- **Rate law:** $v(rate) = k_f\,[N_2O_4]$
- **Reverse reaction:**
  $2\,NO_2\,(g) \longrightarrow N_2O_4\,(g)$
- **Rate law:** $v(rate) = k_r\,[NO_2]^2$

The Equilibrium Constant

- Therefore, at equilibrium

$$v_f = v_r$$

$$k_f\,[N_2O_4] = k_r\,[NO_2]^2$$

- Rewriting this, it becomes

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes:

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

- To generalize this expression, consider the reaction

$$aA + bB \rightleftharpoons cC + dD$$

- The equilibrium expression for this reaction would be

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

What are the equilibrium expressions for these reactions?

$CH_4(g) + H_2(g) \rightleftharpoons CO(g) + 3H_2(g)$;

$$K_{eq} = \frac{[CO][H_2]^3}{[CH_4][H_2]}$$

$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$

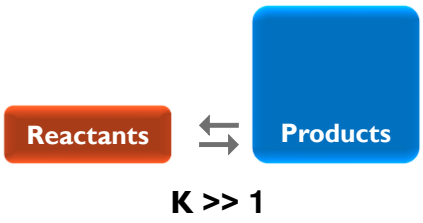
$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

What is the equilibrium expression for this reaction?

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

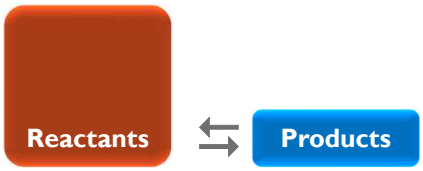
$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

What does the value of *K* mean?



K >> 1

- If *K* >> 1, the reaction is *product-favored*; **product predominates** at equilibrium.
  („eq. lies to the right“)



K << 1

- If K << 1, the reaction is *reactant-favored*; **reactant predominates** at equilibrium.
  („eq. lies to the left“)

Disturbing a Chemical Equilibrium

The equilibrium between reactants and products may be disturbed in three ways:

(1) by changing the **concentration** of a reactant or product

(2) by changing the **temperature**

(3) by changing the **volume** (for systems involving gases)

A change in any of these factors will cause a system at equilibrium to response - ***Le Chatelier's principle.***

Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in *temperature*, *pressure*, or the *concentration* of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."



Henry Louis Le Châtelier
(1850-1936)

„All my life I maintained respect for order and law. Order is one of the most perfect forms of civilization"

- ***The Le Châtelier's principle states that:***
  if a system at equilibrium is disturbed, the position of equilibrium will shift to minimize the disturbance(stress).

Simply said.....

- When you **take** something **away from a system** at equilibrium, the **system shifts** in such a way as **to replace** what you've taken away.

- When you **add** something **to a system** at equilibrium, the **system shifts** in such a way as **to use up** what you've added.

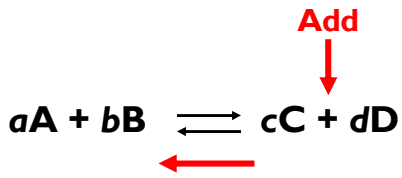
The Effect of Changes in Concentration

Consider general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

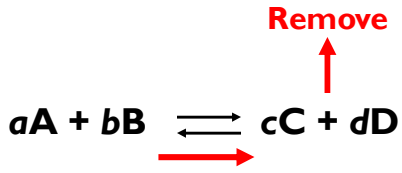
Change	Shifts the Equilibrium

Consider general reaction:



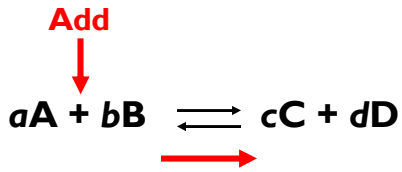
Change	Shifts the Equilibrium
Increase concentration of product(s)	left

Consider general reaction:



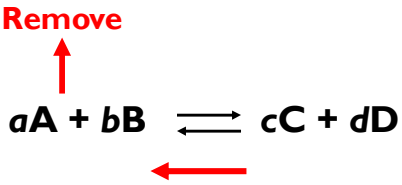
Change	Shifts the Equilibrium
Increase concentration of product(s)	left
Decrease concentration of product(s)	right

Consider general reaction:



Change	Shifts the Equilibrium
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right

Consider general reaction:



Change	Shifts the Equilibrium
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

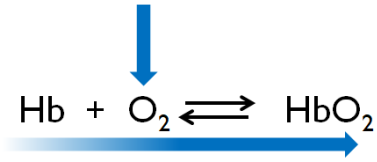
The Le Châtelier principle in physiology

Oxygen Transport

$$Hb + O_2 \leftrightarrows HbO_2$$

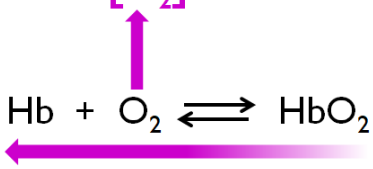
Oxygen Transport

Lungs: high [O_2]



- The equilibrium shifts to the right
- Hb and O_2 combine to make more HbO_2

Muscles: low [O_2]



- The equilibrium shifts to the left
- HbO_2 breaks down (dissociates) increasing the amount of free O_2.

Carbon monoxide poisoning

CO binds to hemoglobin 200 times more tightly than does O_2.

O_2-hemoglobin $\underset{+O_2}{\rightleftarrows}$ hemoglobin $\overset{+CO}{\rightleftarrows}$ CO-hemoglobin

CO poisoning is treated by **administration of pure O_2** which promotes the shift of the above equilibrium to the left. This can be made even more effective by placing the victim in a hyperbaric chamber in which the pressure of O_2 can be made greater than 1 atm.

Effects of Pressure Change on Equilibrium

Consider general reaction:

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g)$$

Change	Shifts the Equilibrium
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

- When the number of gas moles on either side is the same, there is no effect.

Consider the reaction: $\mathbf{N_2(g) + 3H_2(g) \rightleftarrows 2\ NH_3(g)}$

1. The total moles of gas decreases as reaction proceeds in the forward direction.
2. If pressure is increased by decreasing the volume (compression), a forward reaction occurs to reduce the stress.
3. If volume expands and pressure drops, reverse reaction occurs to compensate.

Consider the reaction: $\mathbf{PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)}$

1. The total moles of gas increases as reaction proceeds in the forward direction.
2. If mixture is compressed, pressure increases, and reverse reaction occurs to reduce pressure.
3. If volume expands and pressure drops, forward reaction occurs to compensate.

Reactions not affected by pressure changes

Consider the following reactions:

1. $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$;
2. $H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g)$;

1. Reactions have the same number of gas molecules in reactants and products.
2. Reducing or increasing the volume will cause equal effect on both sides – no net reaction will occur.
3. Equilibrium is not affected by change in pressure.

The Effect of Temperature on Equilibrium

The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- For an **exothermic** reaction - **heat is a product.**
- Increasing the temperature is like adding product.
- Decreasing the temperature is like removing product.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- For an **exothermic** reaction - **heat is a product**.
- Increasing the temperature is like adding product.
- Decreasing the temperature is like removing product.

add heat (increase T)



$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

The Effect of Temperature Changes on Equilibrium for Exothermic Reactions

- For an **exothermic** reaction - **heat is a product.**
- Increasing the temperature is like adding product.
- Decreasing the temperature is like removing product.

remove heat (decrease T)



$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

The Effect of Temperature Changes on Equilibrium for Endothermic Reactions

- For an **endothermic** reaction, **heat is a reactant**
- Increasing the temperature is like adding reactant.
- Decreasing the temperature is like removing reactant.

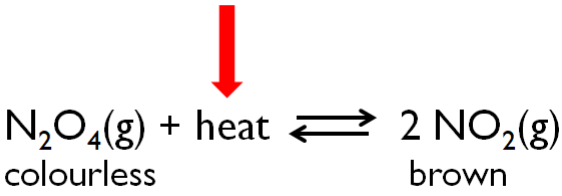
$$N_2O_4(g) + \text{heat} \rightleftharpoons 2\,NO_2(g)$$

colourless — brown

The Effect of Temperature Changes on Equilibrium for Endothermic Reactions

- For an **endothermic** reaction, **heat is a reactant**
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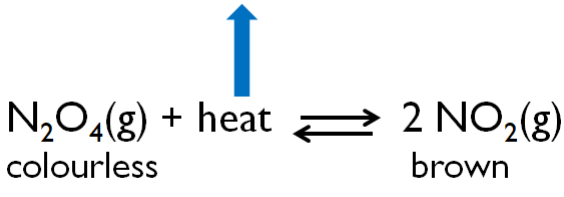
add heat (increase T)



The Effect of Temperature Changes on Equilibrium for Endothermic Reactions

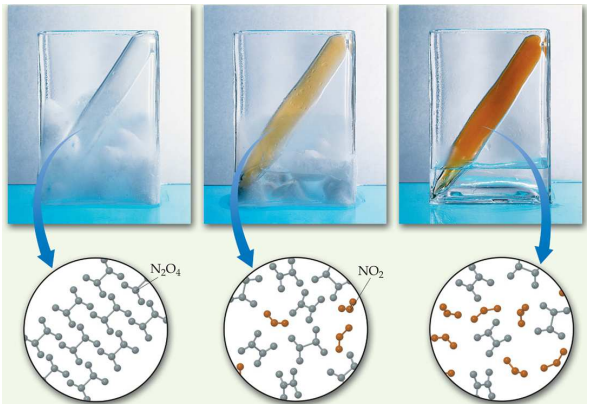
- For an **endothermic** reaction, **heat is a reactant**
- Increasing the temperature is like adding reactant.
- Decreasing the temperature is like removing reactant.

remove heat (decrease T)



Endothermic reaction:

$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$





−196°C 0°C 23°C 35°C 50°C

Equilibrium Exercise #1

Determine whether the following reactions are **favored by high or low pressures?**

1. $2SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$;
2. $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$;
3. $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$;
4. $N_2O_4(g) \rightleftarrows 2\ NO_2(g)$;
5. $H_2(g) + F_2(g) \rightleftarrows 2\ HF(g)$;

Equilibrium Exercise #2

Determine whether the following reactions are **favored by high or low temperatures?**

1. $2SO_{2(g)} + O_{2(g)} \rightleftarrows 2\ SO_{3(g)}$;	ΔH° = -180 kJ/mol
2. $CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)}$;	ΔH° = -46 kJ/mol
3. $CO_{(g)} + Cl_{2(g)} \rightleftarrows COCl_{2(g)}$;	ΔH° = -108 kJ/mol
4. $N_2O_{4(g)} \rightleftarrows 2\ NO_{2(g)}$;	ΔH° = +57 kJ/mol
5. $CO_{(g)} + 2H_{2(g)} \rightleftarrows CH_3OH_{(g)}$;	ΔH° = -270 kJ/mol

Not Changing the Position of Equilibrium: The Effect of Catalysts

- Catalysts affect the rate of the forward and reverse reactions by the same factor.
- Therefore, **catalysts do not affect the position of equilibrium.**
- However, **if a system is NOT at equilibrium**, a catalyst will shorten the time needed to achieve equilibrium

ACIDS & BASES

ACID-BASE BALANCE

BUFFERS



ACIDS & BASES

- A group of chemical properties is related to acidity. According to these properties, a substance can be called an **acid** or a **base**.
- The word **acid** comes from Latin ***acere*** meaning **sour**.
- A **base** is an **alkaline**, which is derived from Arabic ***alqali***.
- **Lavoisier** named **oxygen** as the element from which **acids are derived** (the end of 18th century)
- **Liebig** (German) proposed that an **acid contains hydrogen** (1838)

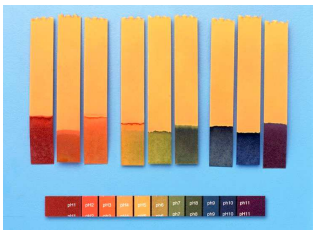
Properties of ACIDS



- Have a sour taste
- Corrosive
- Conduct electricity
- Some acids react strongly with metals
- Turns blue litmus paper red

Properties of BASES

- Have a slippery feeling
- Taste Bitter
- Corrosive
- Can conduct electricity
- Do not react with metals
- Turns red litmus paper blue





Arrhenius acids and bases

Svante August Arrhenius proposed that substances exists as ions in solution in his dissertation, which was awarded a fourth class (**D**) in 1884. He was unable to find a job in his native Sweden.
He was awarded the Nobel Prize in 1903 for his electrolytic dissociation theory. ☺

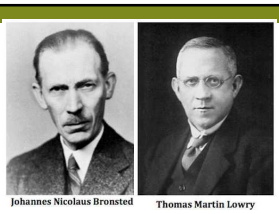
The fundamental concept:

Acid - any substance which delivers hydrogen ion (H^+) to the solution.

$$HA \rightarrow H^+ + A^-$$

Base - any substance which delivers hydroxide ion (OH^-) to the solution.

$$BOH \rightarrow X^+ + OH^-$$


Johannes Nicolaus Bronsted

Thomas Martin Lowry

Brønsted-Lowry theory of acids and bases

An **acid** is a substance from which a proton can be removed.
Acids are proton donors.

A **base** is a substance that can remove a proton from an acid.
Bases are proton acceptors.

Acid-base reactions are competitions for protons.

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$$
$$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^-$$
$$CH_3COOH + H_2O \leftrightarrow H_3O^+ + CH_3COO^-$$
$$H_2O + NH_3 \leftrightarrow NH_4^+ + OH^-$$

conjugate acids and bases

Self-ionization of water

Water molecules autoionize:

$$H_2O + H_2O \longleftrightarrow H_3O^+ + OH^-$$

$$K_{eq} = \frac{[H_3O^+]\times[OH^-]}{[H_2O]^2}$$

$3.24 .\times10^{-18}$ $([H_2O] = 1000/18 = 55.6)$

$$K_w = [H_2O]^2 \times K_{eq} = [H_3O^+]\times[OH^-] = 1\times10^{-14}\ [mol^2.l^{-2}]$$

(only at 25°C, it's *T* dependent)

The **ion product of water**, K_w increases as *T* increases, and its value remains the same in the presence of acid or base.

Solutions of strong acids and bases

Strong acids and **strong bases** **completely ionize in their solutions.** $HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$

$KOH\ (aq) \rightarrow K^+\ (aq) + OH^-\ (aq)$

In a **0.100 M HCl or HNO_3 solution**,

$[H^+] = 0.100$ M

and $[OH^-] = 10^{-14} / 0.100 = 10^{-13}$ M at 25°C

In a **0.100 M NaOH or KOH solution**,

$[OH^-] = 0.100$ M

and $[H^+] = 10^{-14} / 0.100 = 10^{-13}$ M at 25°C

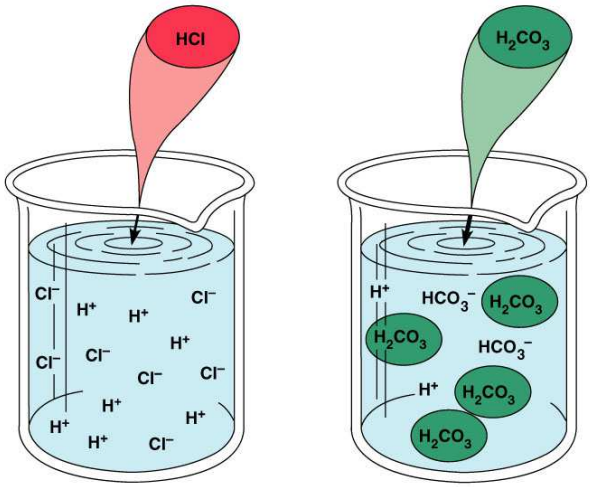
In a **0.010 M $Ca(OH)_2$ solution**,

$[OH^-] = 2\times0.010 = 0.020$ M

$[H^+] = 10^{-14} / 0.020 = 5\times10^{-13}$ M at 25°C

M = mol.l^{-1}

Strong acids vs. Weak acids



100% dissociation into ions

partial dissociation, both ions and molecules

Some strong acids and bases

Strong acids

Hydrogen halides

HCl HBr HI

Oxyacids of halogens

$HClO_3$ $HBrO_3$ HIO_3
$HClO_4$ $HBrO_4$ HIO_4

Other oxyacids

H_2SO_4 HNO_3

Strong Bases

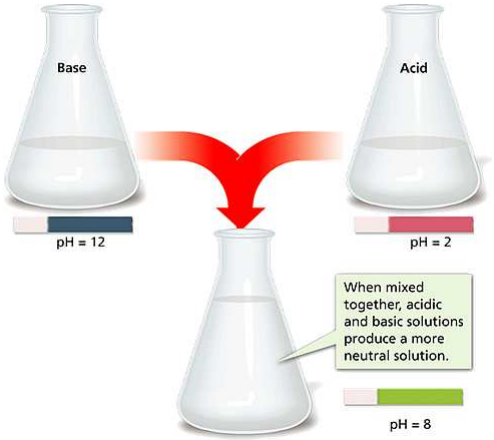
Hydroxides of alkali metals

NaOH KOH CsOH

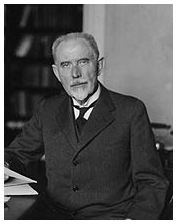
Hydroxides of alkali earth

$Ca(OH)_2$ $Sr(OH)_2$

Neutralization = reaction between an acid and a base (formation of salts)



The pH scale



Søren Peder Lauritz Sørensen introduced the pH scale in 1909. The *p* is from the German word *potenz*, power of (10).

pH = – log [H⁺]; **[H⁺] = 10 $^{-pH}$**

pOH = – log [OH⁻]; **[OH⁻] = 10 $^{-pOH}$**

[H_3O^+] (mol.l^{-1})	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	**10^{-7}**	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	0	1	2	3	4	5	6	**7**	8	9	10	11	12	13	14
[OH^-] (mol.l^{-1})	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	**10^{-7}**	10^{-6}	10^{-5}	10^{-4}	10^{-1}	10^{-2}	10^{-1}	1
pOH	14	13	12	11	10	9	8	**7**	6	5	4	3	2	1	0

A change of **1 pH unit** represents a **tenfold change** in the acidity of the solution.

3 situations can exist for the relative concentrations of hydronium and hydroxide ions in water:

- in ***neutral*** solution, $[H_3O^+] = [OH^-] = 10^{-7}\ mol.l^{-1}$
- in ***acidic*** solutions, $[H_3O^+] > [OH^-]$ $pH < 7$
- in ***basic*** solutions, $[H_3O^+] < [OH^-]$ $pH > 7$

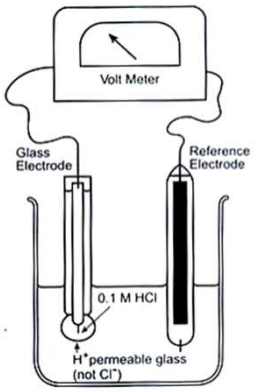
$$pH = -\log [H_3O^+]$$

$$pOH = -\log [OH^-]$$

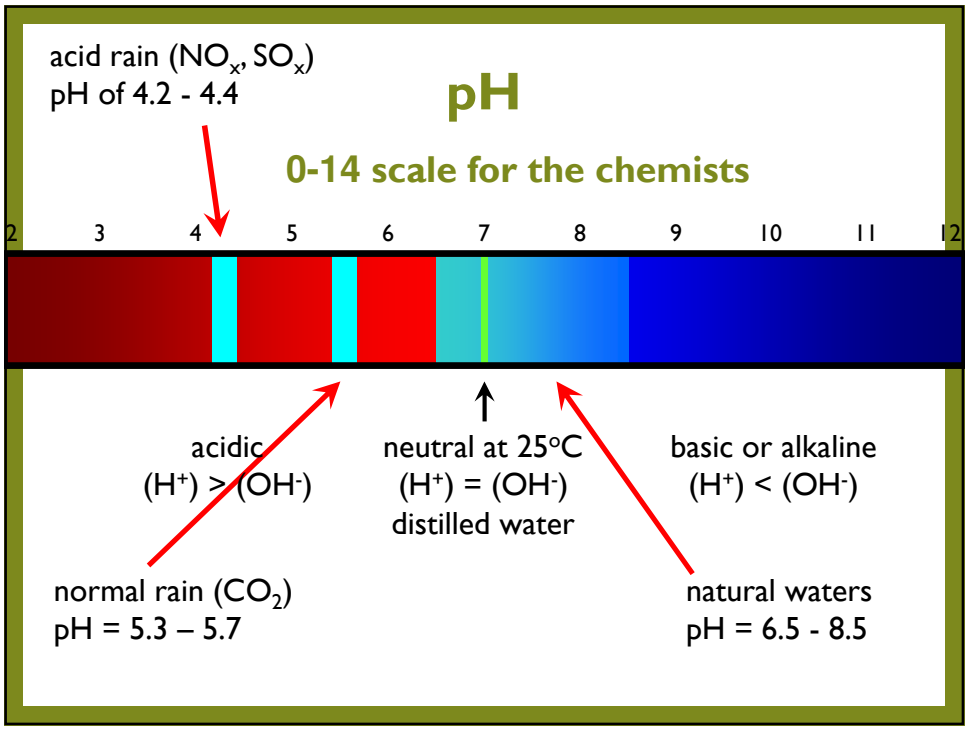
$$pH + pOH = 14$$

pH meter and pH electrodes

The pH meter is based on the principle of measurement of potential between pH-responsive electrode and reference electrode.....







What is acid rain?

Dissolved carbon dioxide lowers the pH

$$CO_2\,(g) + H_2O \leftrightarrows H_2CO_3 \leftrightarrows H^+ + HCO_3^-$$

Atmospheric pollutants from combustion

$$NO, NO_2 + H_2O \ldots \rightarrow HNO_3$$

$$SO_2, SO_3 + H_2O \ldots \rightarrow H_2SO_4$$

both strong acids

pH < 5.3

Ionization of weak acids

$$HA + H_2O \longleftrightarrow H_3O^+ + A^-$$

↑ Weak acid — ↑ Conjugate base

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

acidity constant

The pK_a is defined similar to the pH: $pK_a = -\log K_a$

$K_a = 10^{-pKa}$

Ionization of weak bases

$$B + H_2O \longleftrightarrow BH^+ + OH^-$$

↑ Weak base — ↑ Conjugate acid

$$K_b = K_{eq}[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

basicity constant

The pK_b is defined similar to the pK_a:

$pK_b = -\log K_b$ $\quad K_b = 10^{-pKb}$

Some weak acids and bases

Common Weak Acids	
Formic acid	$HCOOH$
Acetic acid	CH_3COOH
Trichloroacetic acid	CCl_3COOH
Hydrofluoric	HF
Hydrocyanic	HCN
Hydrogen sulfide	H_2S
Water	H_2O

Common Weak Bases	
Ammonia	NH_3
Trimethyl ammonia	$N(CH_3)_3$
Pyridine	C_5H_5N
Ammonium hydroxide	NH_4OH
Water	H_2O
HS^- ion	HS^-

The hydrolysis of salts

The origin of the salt	Hydrolysis occurs	Hydrolyzing ion	pH of a solution
Strong acid + strong base	no	none	**7**
Strong acid + weak base	yes	cation	**< 7**
Weak acid + strong base	yes	anion	**> 7**
Weak acid + weak base	yes	cation + anion	**≈ 7**

The hydrolysis of salts

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Weak acid + strong base	yes	anion	**> 7**
Weak acid + weak base	yes	cation + anion	**≈ 7**

Explanation:

$$NH_4Cl \longleftrightarrow NH_4^+ + Cl^-$$

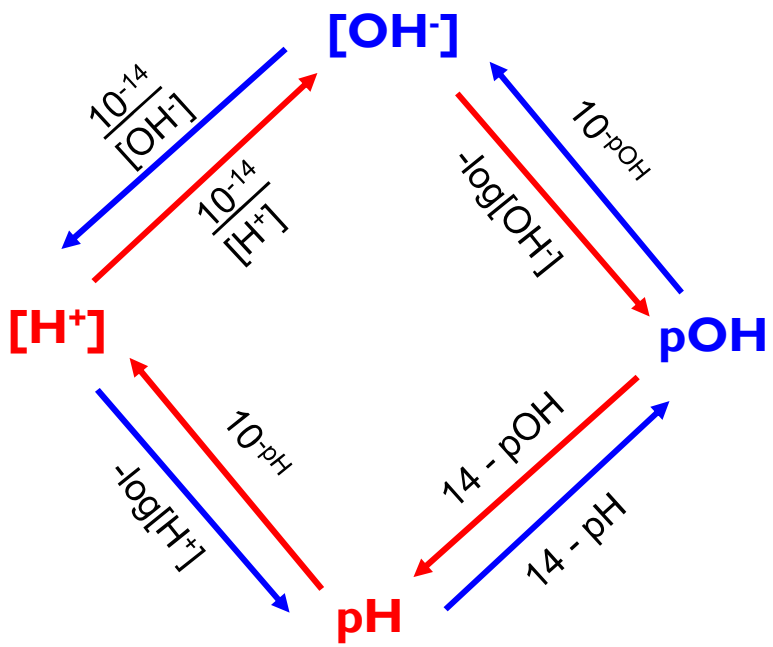
Anion of this salt (Cl^-) comes from the strong acid (HCl), it does not react with water, and is found in the hydrated form in the solution.

Cation of this salt is the subject of hydrolysis:

$$NH_4^+ + H_2O \longleftrightarrow NH_3 + H_3O^+$$

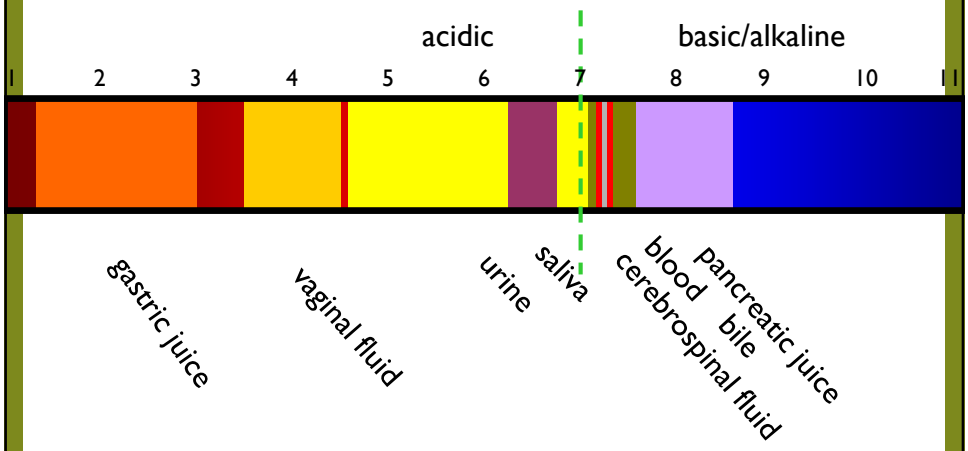
Calculation of pH – formulas:

strong acid	$pH = - \log [H_3O^+]$
strong base	$pOH = - \log [OH^-]$ $pH = 14 - pOH$
weak acid	$pH = ½ pK_a - ½ \log c_a$
weak base	$pOH = ½ pK_b - ½ \log c_b$ $pH = 14 - ½ pK_b + ½ \log c_b$



pH

The biological view in the human body



Tortora & Grabowski, *Prin. of Anatomy & Physiology*, 10th ed., Wiley (2003)

pH values of some cells and body fluids

Body cells	pH	Body fluids	pH
Erythrocytes	7.00	Blood	7.36 – 7.44
Platelets	7.28	Gastric juice	1.00 – 2.00
Osteoblasts	8.50	Duodenal juice	6.50 – 7.60
Prostatic cells	4.50	Urine	5.00 – 8.00
Sceletal muscle cells	6.90	Bile	6.20 – 8.50
		Saliva	7.00 – 7.50
		Pancreatic juice	7.50 – 8.80

The Body and pH

- Homeostasis of pH is tightly controlled
- Extracellular fluid = 7.4
- Blood = 7.36 – 7.44
  < 6.8 or > 8.0 death occurs
- pH below 7.36 = **Acidemia**
- pH above 7.44 = **Alkalemia**

Small changes in pH can produce major disturbances

- Change of enzymes activity
- Change of metabolism
- Effect on electrolytes
- Failure of function of excitable tissues (muscle, heart, nervous system)

The body produces more acids than bases

- Acids from diet
- Acids produced by metabolism of lipids and proteins
- Cellular metabolism produces CO_2

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \leftrightarrows H^+ + HCO_3^-$$

Control of pH in organism

- **chemical buffer systems (buffers)**
- **respiratory system (lungs)**
- **urinary system (kidneys)**

BUFFER SYSTEMS

Composition:

- *Mixture of a weak acid and salt of its conjugate base*
- *Mixture of a weak base and salt of its conjugate acid*

Function:

- maintaining the pH of a solution constant by taking up protons that are released during reactions, or by releasing protons when they are consumed by reactions

BUFFER SYSTEMS

Composition:

- *Mixture of a weak acid and salt of its conjugate base*
- *Mixture of a weak base and salt of its conjugate acid*

Function:

- maintaining approximately constant pH upon small additions of acid or base.

Mechanism of buffer action

ACETATE BUFFER = Mixture of a weak acid and salt of its conjugate base = **CH_3COOH and $CH_3COO^-Na^+$**

Addition of a strong acid (HCl):

$$CH_3COOH + CH_3COO^- + Na^+ + HCl \longrightarrow 2CH_3COOH + NaCl$$

Addition of a strong base (NaOH):

$$CH_3COOH + CH_3COO^- + Na^+ + NaOH \longrightarrow 2CH_3COO^- + 2Na^+ + H_2O$$

Buffer capacity

= ***the quantity of strong acid (or base) that has to be added to one liter of a buffer solution to change its pH value by one unit.***

Calculation of buffer pH

(Weak **acid** + **salt** of its conjugate base)

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

↑ Weak acid — ↑ Conjugate base

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Calculation of buffer pH

(Weak **acid** + **salt** of its conjugate base)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

$$-\log [H_3O^+] = -\log \left(K_a \times \frac{[HA]}{[A^-]}\right) = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Henderson-Hasselbalch equation

Calculation of buffer pH

(Weak **acid** + **salt** of its conjugate base)

Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Calculation of buffer pH

(Weak **base** + **salt** of its conjugate acid)

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

$pH = 14 - pOH$ $\quad pH = 14 - (pK_b + \log \frac{[salt]}{[base]})$

$$pH = 14 - pK_b - \log \frac{[salt]}{[base]}$$

$$pH = 14 - pK_b + \log \frac{[base]}{[salt]}$$

Buffers in biological systems and their primary roles

Buffer system	Major function
Bicarbonate (H_2CO_3 / HCO_3^-)	Primary ECF buffer against non-carbonic acid changes
Protein (protein / proteinate)	Primary ICF buffer; also buffers ECF
Hemoglobin (Oxyhemoglobin / hemoglobin)	Primary buffer against carbonic acid changes
Phosphate ($H_2PO_4^-$ / HPO_4^{2-})	Important urinary buffer; also buffers ICF

Effect of bicarbonate buffer system

(salt) $NaHCO_3 / H_2CO_3$ *(acid)*

(salt)

$H^+ Cl^-$ + $NaHCO_3$ + H_2CO_3 ⟶ $NaCl$ + H_2CO_3 + H_2CO_3

(acid)

$Na^+ OH^-$ + H_2CO_3 + $NaHCO_3$ ⟶ $NaHCO_3$ + H_2O + $NaHCO_3$

Effect of bicarbonate buffer system

(salt) $NaHCO_3 / H_2CO_3$ *(acid)*

(salt)

$H^+ Cl^-$ + $NaHCO_3$ + H_2CO_3 ⟶ $NaCl$ + 2 H_2CO_3

(acid)

$Na^+ OH^-$ + H_2CO_3 + $NaHCO_3$ ⟶ 2 $NaHCO_3$ + H_2O

Bicarbonate buffer system

$$pH = pK_a + \log \frac{[NaHCO_3]}{[H_2CO_3]}$$

Henderson – Hasselbalch equation

- $pK_a = 6.1$
- $[HCO_3^-] = 24$ mmol.l^{-1}
- $[H_2CO_3] = 1.2$ mmol.l^{-1}

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 20$$

Bicarbonate buffer system

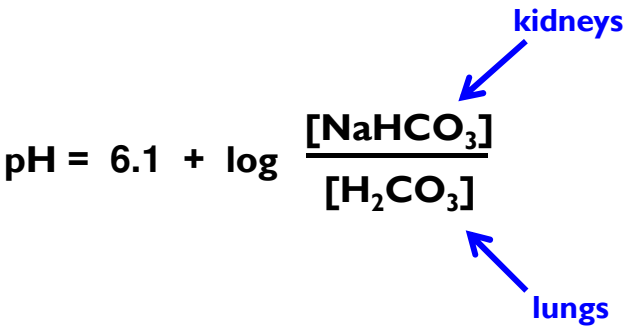
$$pH = pK_a + \log \frac{[NaHCO_3]}{\alpha\, pCO_2}$$

Henderson – Hasselbalch equation

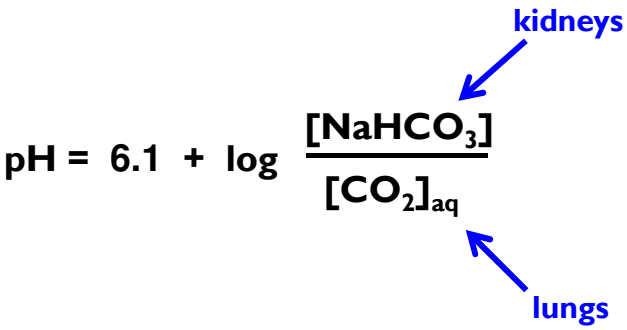
- $pK_a = 6.1$
- $[HCO_3^-] = 24$ mmol.l^{-1}
- $\alpha = 0.224$ mmol.l^{-1} / kPa $pCO_2 = 5.3$ kPa

Buffering the changes of pH in organism causes changes of concentrations of HCO_3^- a H_2CO_3

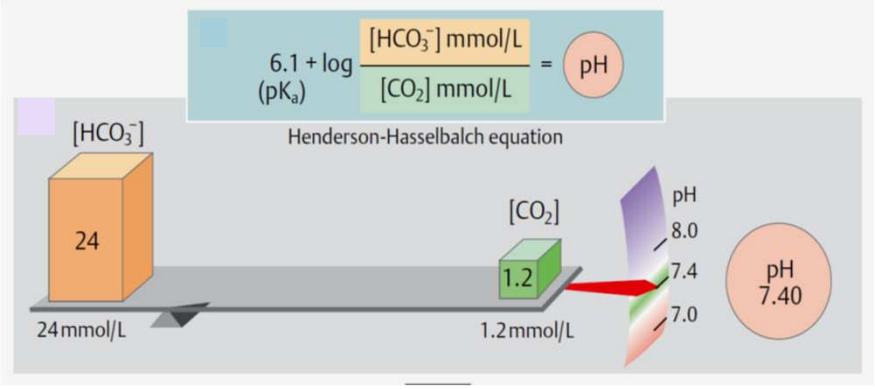
Bicarbonate buffer system

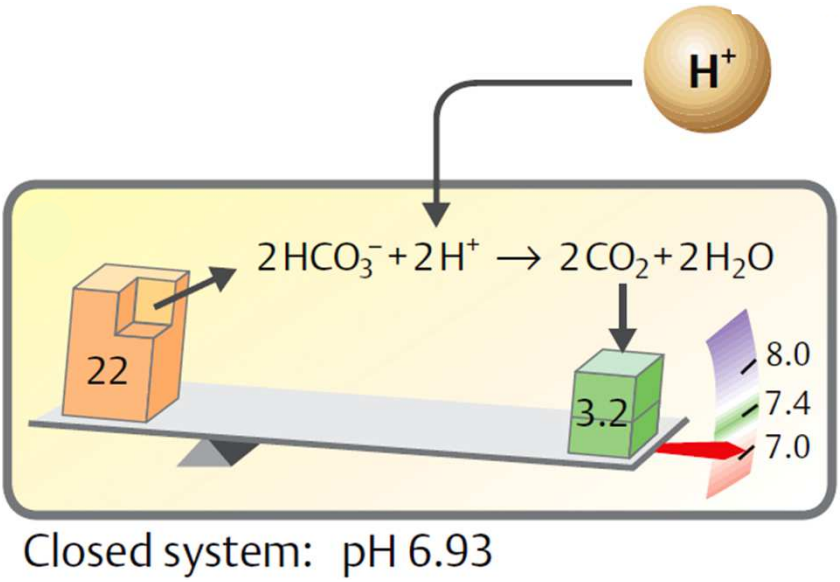


Bicarbonate buffer system

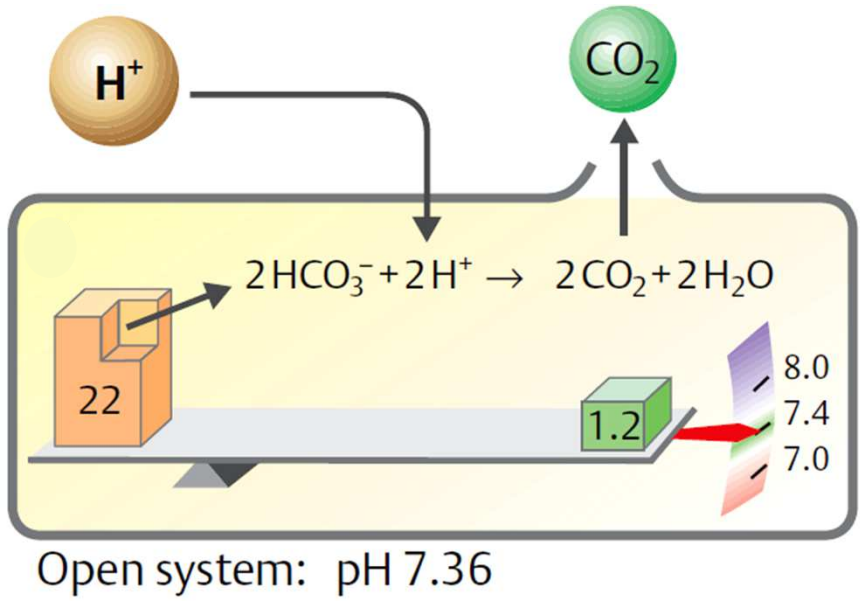


Bicarbonate buffer system





Closed system: pH 6.93



Lungs

- Concentration of carbonic acid is proportional to the value of pCO_2
- ***pCO_2 is dependent on lungs function***
- H_2CO_3 = pCO_2 x 0.225 (mmol/l)

Kidney

- ***Reabsorption of $NaHCO_3$*** in kidney tubules
- ***Regeneration of $NaHCO_3$*** in kidney
- If needed – excretion of $NaHCO_3$

Disorders of ABB

- **Acidosis** = excess of acid (accumulation of acids or loss of bases)
- **Alkalosis** = excess of bases (accumulation of bases or more often loss of acids)

- **Acidemia** = blood pH < 7.36
- **Alkalemia** = blood pH > 7.44

Disorders of ABB

- Metabolic and respiratory
- Primary and secondary
- Acute and chronic
- Simple and combined

Disorders of ABB

- Metabolic and respiratory
- Primary and secondary
- Acute and chronic
- Simple and combined

Metabolic disorders

ACIDOSIS (decrease) **ALKALOSIS** (increase)

$$pH = 6.1 + \log \frac{[NaHCO_3]}{[H_2CO_3]}$$

Respiratory disorders

$$pH = 6.1 + \log \frac{[NaHCO_3]}{[H_2CO_3]}$$

(increase) **ACIDOSIS**

(decrease) **ALKALOSIS**

Phosphate buffer system

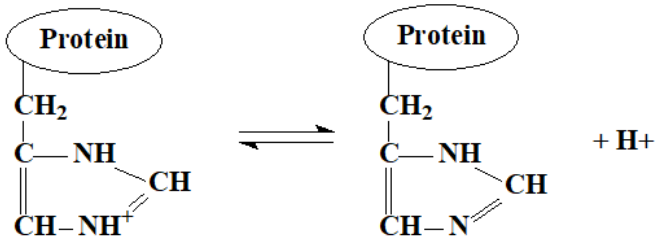
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

weak acid — conjugate base

• Important **in urine** and intracellular buffering systems. The excess phosphate filtered through the kidneys is not reabsorbed but remains in the tubular fluid to be excreted.
This excreted phosphate buffers urine as it is being formed by removing from solution the H^+ secreted into the tubular fluid.

Protein buffer system

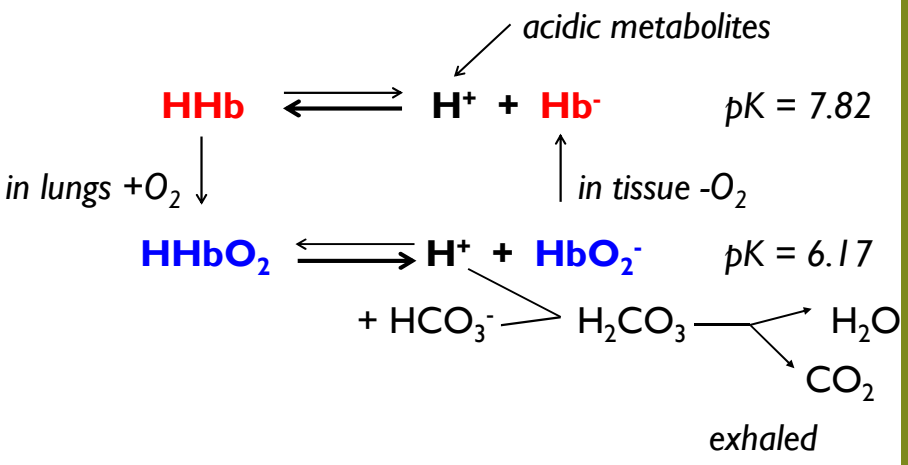
imidazole groups of histidine



sulfhydryl groups of cysteine

$$R{-}SH \longleftrightarrow R{-}S^{-} + H^{+}$$

Hemoglobin buffer system



Oxyhemoglobin is stronger acid than deoxyhemoglobin.