

الباب الرابع الأحماض والقواعد

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النظريات الحديثة لتعريف الأحماض والقواعد :

(Lavoisier)

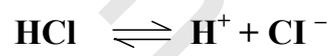
(Binary Compounds)

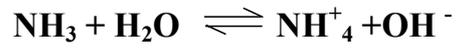
(Acid radical)

(Humphry Davy)

(Arrhenius)

: (Faraday)
(Electrolytes)





أسباب قصور نظرية أرهينيوس :

:

:

:

H^+

:

10^{-6}

10^{-8}

H^+

/ 300 (Exothermic)

10^{-19}

H^+

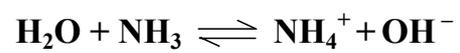
H^-

H^+

تعريف أخرى للحامض والقاعدة :

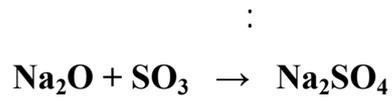
(Lowry)

(Bronsted)



(Lewis)

: (Usanovich)

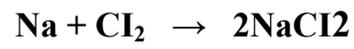


O^{-2}

SO_3

Na_2SO_4

Na_2O



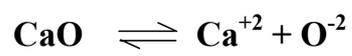
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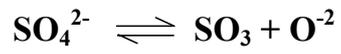


CN^-

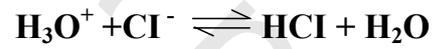
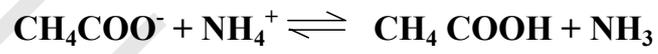
CN^-

(Lux)





نظرية برونستد – لوري Bronsted – Lowry Theory :





:



(acid₁)

(base₁)

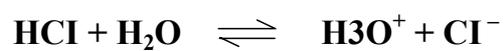
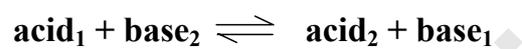
(base₂)

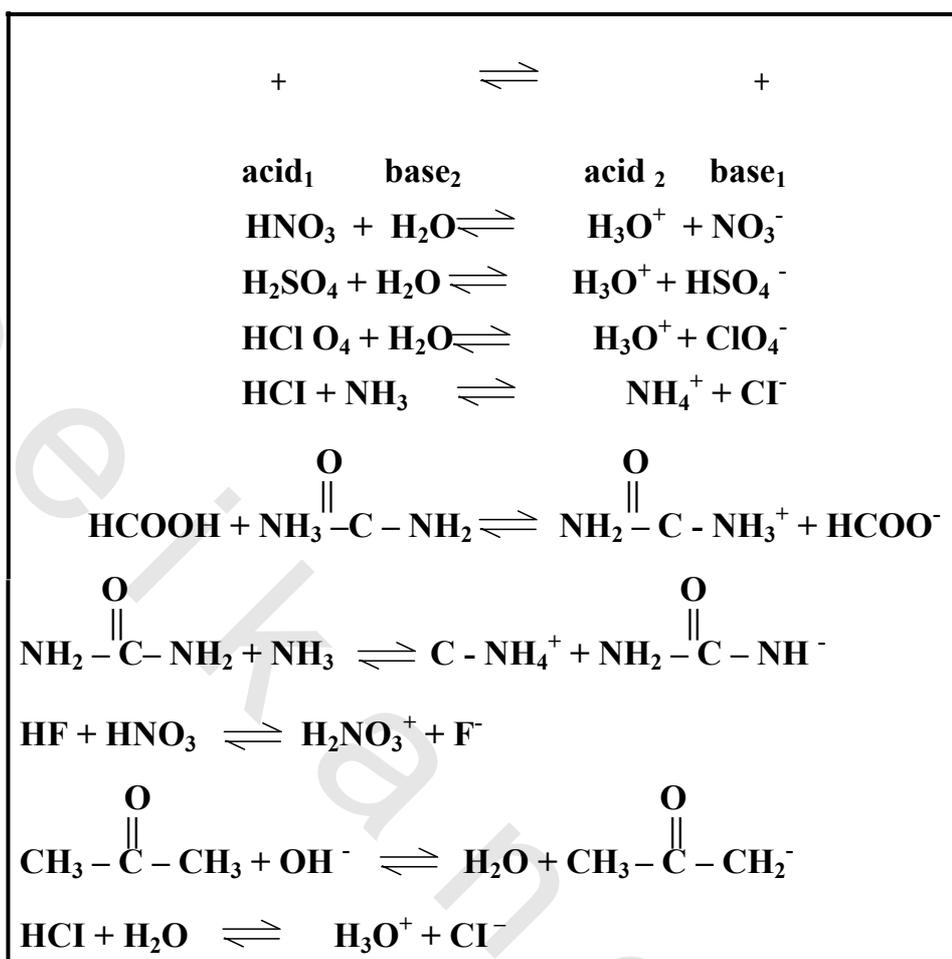
(acid₂)

+

\rightleftharpoons

+





القوى النسبية للأحماض والقواعد :

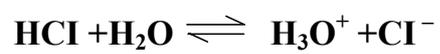


بديهيات نظرية برونستد :

+



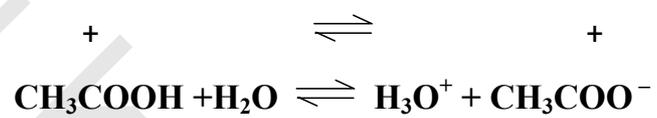
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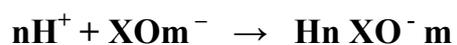
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HClO_4

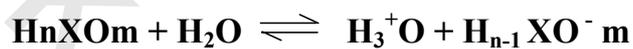
قوة الأحماض الأوكسجينية : Strength of Oxyacids :

:

(Oxyanions)



:



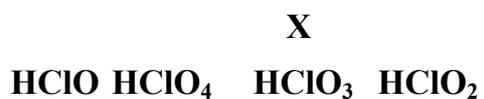
n+



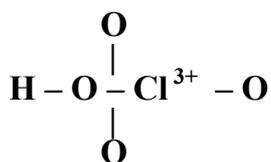
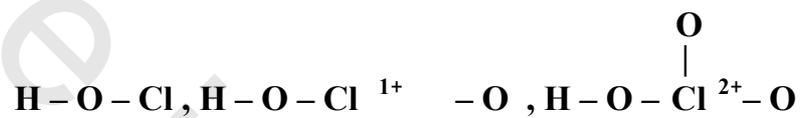
×

X (Inductive effect)

O-H



: 3+ 2+ 1+



7+ 5+ 3+ 1+

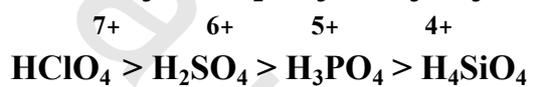
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:



:



(Pauling)

:

:

10^5

$$1.1 \times 10^{-12} = K_3 \quad 6.2 \times 10^{-8} = K_2 \quad 7.5 \times 10^{-3} = K_1$$

K

$$p \quad pK = - \log K \quad pK$$

$$10 \quad \text{Power}$$

$$(5) \quad pK$$

$$12.327 = pK_3 \quad 7.207 = pK_2 \quad 2.160 = pK_1$$

pK

H₃PO₃

$$7 = pK_2 \quad 1 \times 10^{-7} = K_2 \quad 1.92 = pK_1 \quad 1.2 \times 10^{-2} = K_1$$

$$6.69 = pK_2 \quad 2.0 = pK_1 \quad H_3PO_3$$

:

XO_m(OH)_n

m × n

:

$$2 = pK \quad 1 = m$$

$$7 = pK \quad 0 = m$$

$$8- = pK \quad 3 = m$$

$$3- = pK \quad 2 = m$$

:

$$= m \quad -1$$

H₄SiO₄

B(OH)₃

H₃BO₃



- . 1 = m -2
- . 2 = m -3
- . 3 = m -4

:

	K	pK	
HOCI ClO. (OH) ₁	2.2×10^{-8}	7.4	
HOCIO ClO ₁ (OH) ₁	1.1×10^{-2}	2, -	
HOCIO ₂ ClO ₂ (OH) ₁		1, -	
HOCIO ₃ ClO ₃ (OH) ₁		10 -	



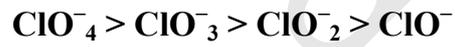
:

الحامض	pK
HOH	16
HOI	11
HOBr	8.7
HOCl	7.4

:

ثابت التأيين	الحامض
$10^{-8} \times 3.2$	HClO
$10^{-2} \times 1.1$	HClO ₂
كبير	HClO ₃
كبير جداً	HClO ₄

:



:

:



:

m

الحامض	الصيغة العامة	قيم m
HClO ₄	HOCIO ₃	3
H ₃ BO ₃	B (OH) ₃	صفر
H ₂ SO ₃	SO (OH) ₂	1
H ₂ SO ₄	(OH) ₂ SO ₂	2

:



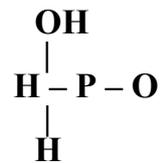
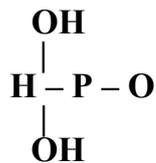
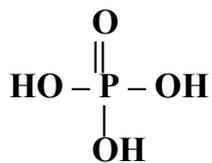
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:

الحامض	الصيغة
حامض الفوسفوريك H ₃ PO ₄	ثلاثي القاعدية PO (OH) ₃
حامض الفوسفوروز H ₃ PO ₃	ثنائي القاعدية HPO (OH) ₂
حامض الهايبوفوسفوروز H ₃ PO ₂	أحادي القاعدية H ₂ PO (OH)

:



pK

(J.Ricci)

$$\text{pK} = 8.0 - m (9.0) + n (4.0)$$

: n :

: m

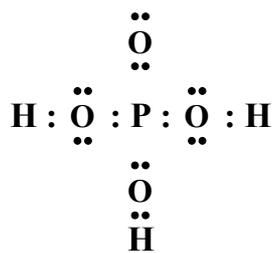
: m

()

(non - bonding electrons)

()

pK₁



$$n = 1$$

$$(\quad 8 \quad)$$

$$4$$

$$: m$$

$$3 = (4) 1 + (9) 1 - 8 = pK_1$$

$$1 = 4 - 5 = m$$

$$2.2$$

$$pK$$

:



$$pK$$

:

$$= n$$

$$2 / 2 = 1$$

$$6$$

$$7 = 1 + 6$$

:

$$m$$

$$7$$

$$8 = pK \therefore$$

$$(4) + (9) 0 - 8 = pK$$

$$= 7 - 7 = m$$

$$7.4$$

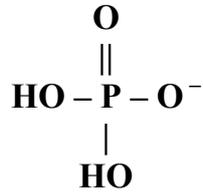
:

$$. pK_3 \quad pK_2 \quad pK_1 :$$

:

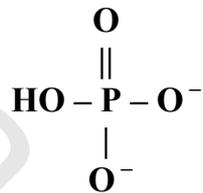
 pK_1

. (3)

: $H_2PO_4^-$ pK_2 

$$7 = pK_2 \quad 1 = m \quad (4) \quad 2 + (9) \quad 1 - 8 = pK_2 \quad 2 = m$$

(7.2)

: pK_3 

$$3 = m$$

$$11 = (4) \quad 3 + (9) \quad 1 - 8 = pK \therefore 1 = m$$

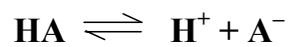
(12)

علاقة التركيب بالحامضية :

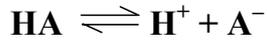
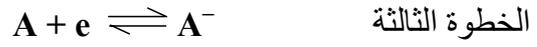
 H^+

HA

:

 A^- 

:



HA

H⁺

. A⁻

A

H-

HA

() A

() A

:

H-A

HA

()

HA

A

()

H-A

)

HA

. (A

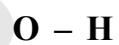
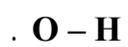
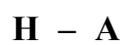
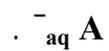
HA

HA

(Solvation)

. A⁻

H₃O⁺



O-H

O-H

:

$O_2NOH > ONOH$

$O_2S(OH)_2 > OS(OH)_2$

:

HF

HI

:

H-F

/

71

H-I

/

71

/

132

.

/ 79

61

H-F H-I

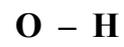
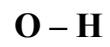
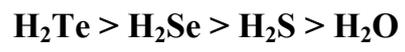
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8

/

:

$HI > HBr > HCl > HF$



O-H

O-H

O₃ClOH

ClOH OClOH O₂ClOH

O-H

CF₃COOH

:

CCl₃COOH

:

CF₃COOH > CCl₃COOH > CCl₂HCOOH >
CClH₂COOH > CH₃COOH

* * *

الأسئلة

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