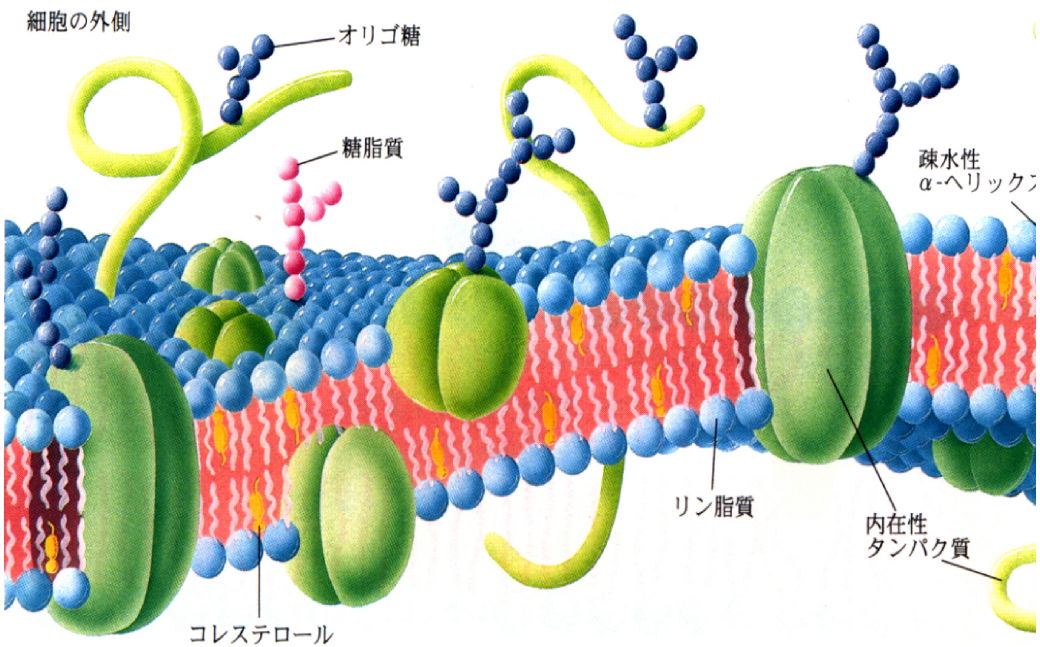
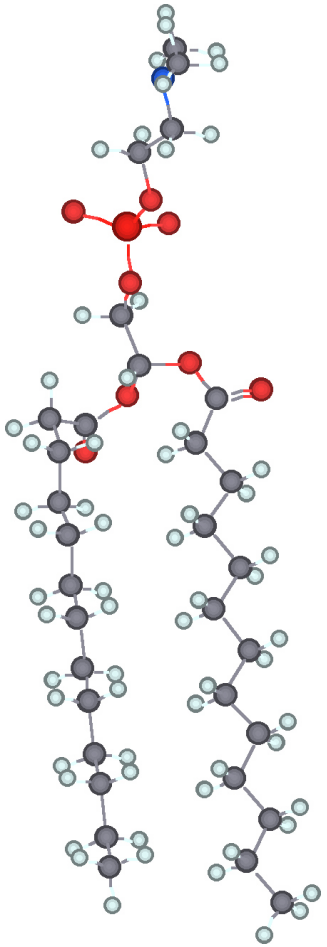
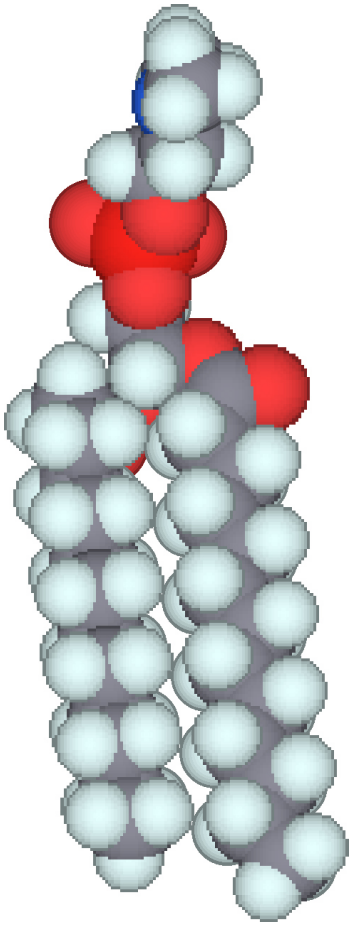
Chapter 22

Amino Acids, Peptides, and Proteins







細胞膜とリン脂質の構造

Amino acid
アミノ酸とは？

正確にはα－アミノカルボン酸

β－アミノ酸？

ω－アミノ酸？

pK_a

アミノ酸の解離状態は

酸解離定数で理解しよう

pH と pK_a の関係

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

平衡定数K_aは、$K_a = [H^+][A^-] / [HA]$

$-\log K_a = -\log([H^+][A^-] / [HA])$

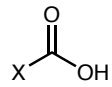
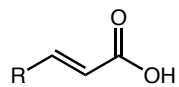
$-\log K_a = -\log[H^+] + -\log([A^-]/[HA])$

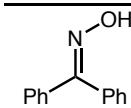
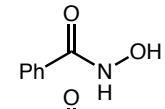
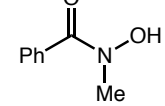
$pH = -\log[H^+]$ 、$pH = -\log[H^+]$ 、と定義すると、

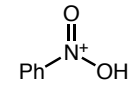
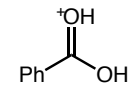
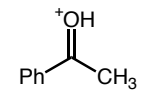
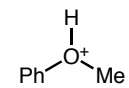
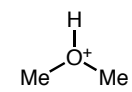
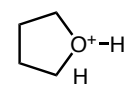
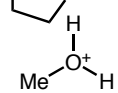
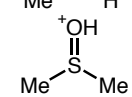
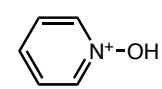
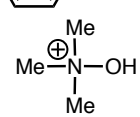
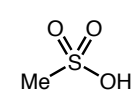
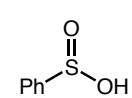
$pK_a = pH - \log([A^-]/[HA])$

※ $[A^-]=[HA]$ の時、$\log([A^-]/[HA])=0$

Substrate	pKa H_2O	(DMSO)
INORGANIC ACIDS		
H_2O	15.7	(32)
H_3O^+	-1.7	
H_2S	7.00	
HBr	-9.00	(0.9)
HCl	-8.0	(1.8)
HF	3.17	(15)
HOCl	7.5	
$HClO_4$	-10	
HCN	9.4	(12.9)
HN_3	4.72	(7.9)
HSCN	4.00	
H_2SO_3	1.9, 7.21	
H_2SO_4	-3.0, 1.99	
H_3PO_4	2.12, 7.21, 12.32	
HNO_3	-1.3	
HNO_2	3.29	
H_2CrO_4	-0.98, 6.50	
CH_3SO_3H	-2.6	(1.6)
CF_3SO_3H	-14	(0.3)
NH_4Cl	9.24	
$B(OH)_3$	9.23	
HOOH	11.6	

Substrate	pKa H_2O	(DMSO)
CARBOXYLIC ACIDS		
		
X= CH_3	4.76	(12.3)
CH_2NO_2	1.68	
CH_2F	2.66	
CH_2Cl	2.86	
CH_2Br	2.86	
CH_2I	3.12	
$CHCl_2$	1.29	
CCl_3	0.65	
CF_3	-0.25	
H	3.77	
HO	3.6, 10.3	
C_6H_5	4.2	(11.1)
o-$O_2NC_6H_4$	2.17	
m-$O_2NC_6H_4$	2.45	
p-$O_2NC_6H_4$	3.44	
o-ClC_6H_4	2.94	
m-ClC_6H_4	3.83	
p-ClC_6H_4	3.99	
o-$(CH_3)_3N^+C_6H_4$	1.37	
p-$(CH_3)_3N^+C_6H_4$	3.43	
p-$OMeC_6H_4$	4.47	
		
R= H	4.25	
trans-CO_2H	3.02, 4.38	
cis-CO_2H	1.92, 6.23	

Substrate	pKa H_2O	(DMSO)
ALCOHOLS		
HOH	15.7	(31.2)
MeOH	15.5	(27.9)
i-PrOH	16.5	(29.3)
t-BuOH	17.0	(29.4)
c-hex_3COH	24.0	
CF_3CH_2OH	12.5	(23.5)
$(CF_3)_2CHOH$	9.3	(18.2)
C_6H_5OH	9.95	(18.0)
m-$O_2NC_6H_4OH$	8.4	
p-$O_2NC_6H_4OH$	7.1	(10.8)
p-$OMeC_6H_4OH$	10.2	(19.1)
2-napthol		(17.1)
OXIMES & HYDROXAMIC ACIDS		
	11.3	(20.1)
	8.88 (NH)	(13.7)
		(18.5)
PEROXIDES		
MeOOH	11.5	
CH_3CO_3H	8.2	

Substrate	pKa H_2O	(DMSO)
PROTONATED SPECIES		
	-12.4	
	-7.8	
	-6.2	
	-6.5	
	-3.8	
	-2.05	
	-2.2	
	-1.8	
	0.79	(+1.63)
		(+5.55)
SULFINIC & SULFONIC ACIDS		
	-2.6	
	2.1	

*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

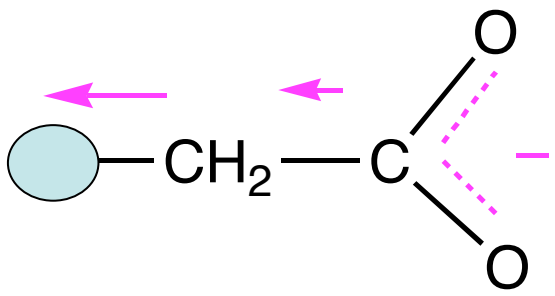
For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

Substrate	pKa H_2O	(DMSO)
INORGANIC ACIDS		
H_2O	15.7	(32)
H_3O^+	-1.7	
H_2S	7.00	
HBr	-9.00	(0.9)
HCl	-8.0	(1.8)
HF	3.17	(15)
HOCl	7.5	
$HClO_4$	-10	
HCN	9.4	(12.9)
HN_3	4.72	(7.9)
HSCN	4.00	
H_2SO_3	1.9, 7.21	
H_2SO_4	-3.0, 1.99	

Substrate	pKa H_2O	(DMSO)
ALCOHOLS		
HOH	15.7	(31.2)
MeOH	15.5	(27.9)
i-PrOH	16.5	(29.3)
t-BuOH	17.0	(29.4)
c-hex_3COH	24.0	
CF_3CH_2OH	12.5	(23.5)
$(CF_3)_2CHOH$	9.3	(18.2)
C_6H_5OH	9.95	(18.0)

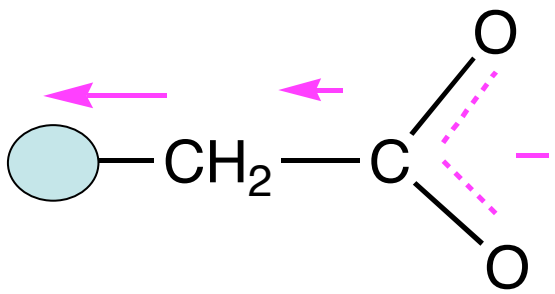
置換基によるpK_aの差異

	pK_a
CH_3COOH	4.8
$ClCH_2COOH$	2.8
$ClCH_2CH_2COOH$	4.1
$ClCH_2CH_2CH_2COOH$	4.5
$ClCH_2CH_2CH_2CH_2COOH$	4.7
$Cl_2CHCOOH$	1.3
Cl_3CCOOH	0.7
FCH_2COOH	2.6



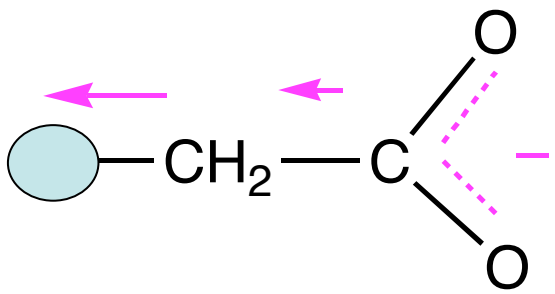
置換基によるpK_aの差異

	pK_a
CH_3COOH	4.8
$ClCH_2COOH$	2.8
$ClCH_2CH_2COOH$	4.1
$ClCH_2CH_2CH_2COOH$	4.5
$ClCH_2CH_2CH_2CH_2COOH$	4.7
$Cl_2CHCOOH$	1.3
Cl_3CCOOH	0.7
FCH_2COOH	2.6



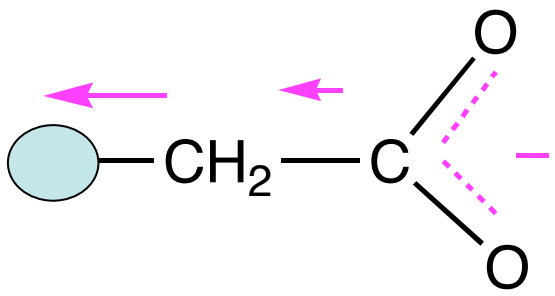
置換基によるpK_aの差異

	pK_a
CH_3COOH	4.8
$ClCH_2COOH$	2.8
$ClCH_2CH_2COOH$	4.1
$ClCH_2CH_2CH_2COOH$	4.5
$ClCH_2CH_2CH_2CH_2COOH$	4.7
$Cl_2CHCOOH$	1.3
Cl_3CCOOH	0.7
FCH_2COOH	2.6



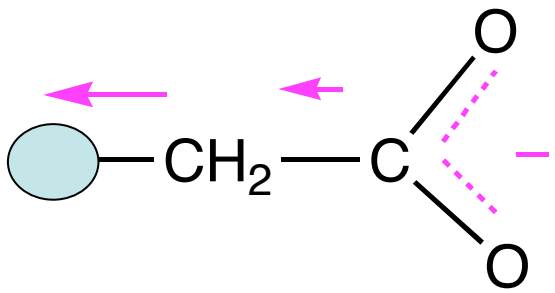
置換基によるpK_aの差異

	pK_a
CH_3COOH	4.8
$ClCH_2COOH$	2.8
$ClCH_2CH_2COOH$	4.1
$ClCH_2CH_2CH_2COOH$	4.5
$ClCH_2CH_2CH_2CH_2COOH$	4.7
$Cl_2CHCOOH$	1.3
Cl_3CCOOH	0.7
FCH_2COOH	2.6

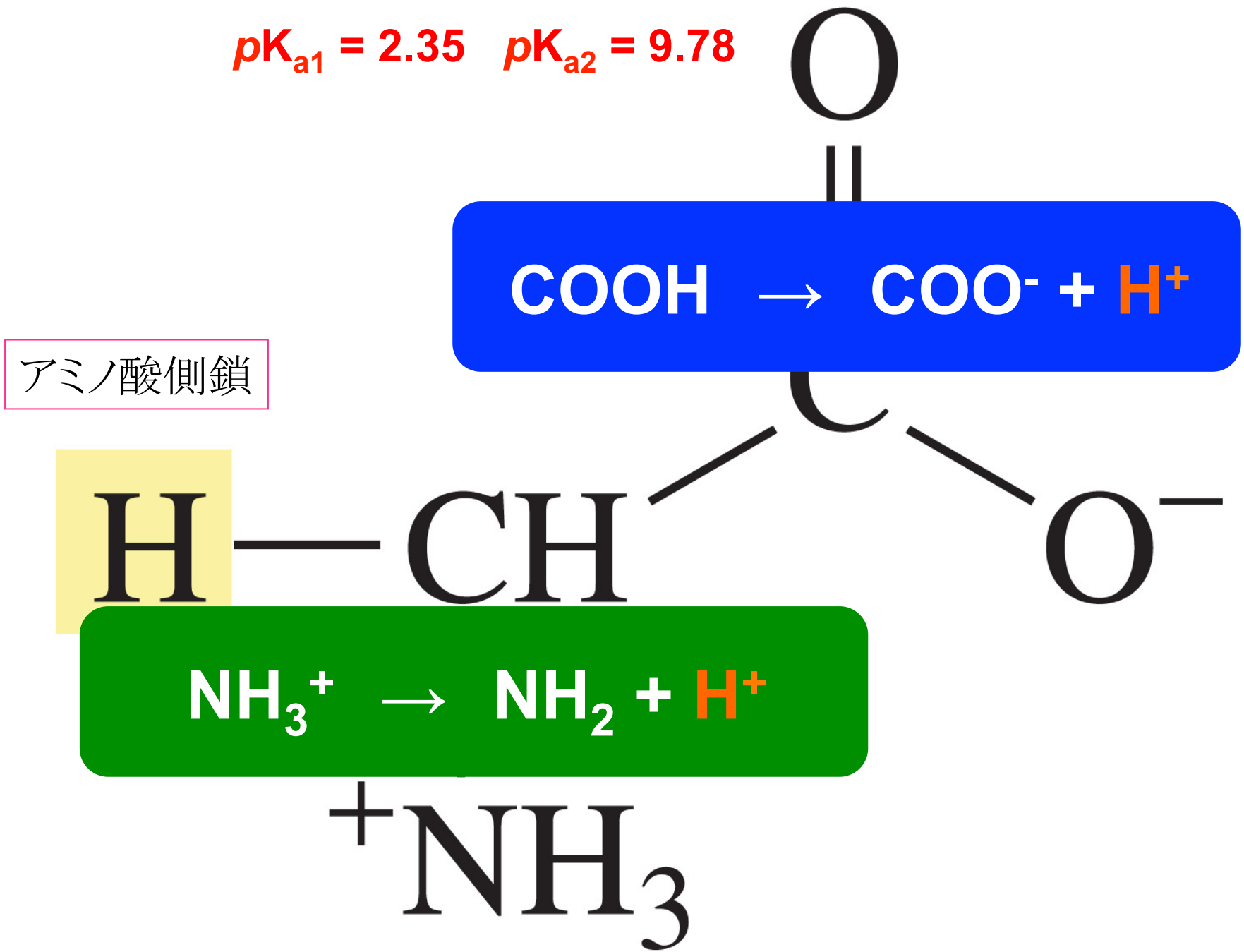


置換基によるpK_aの差異

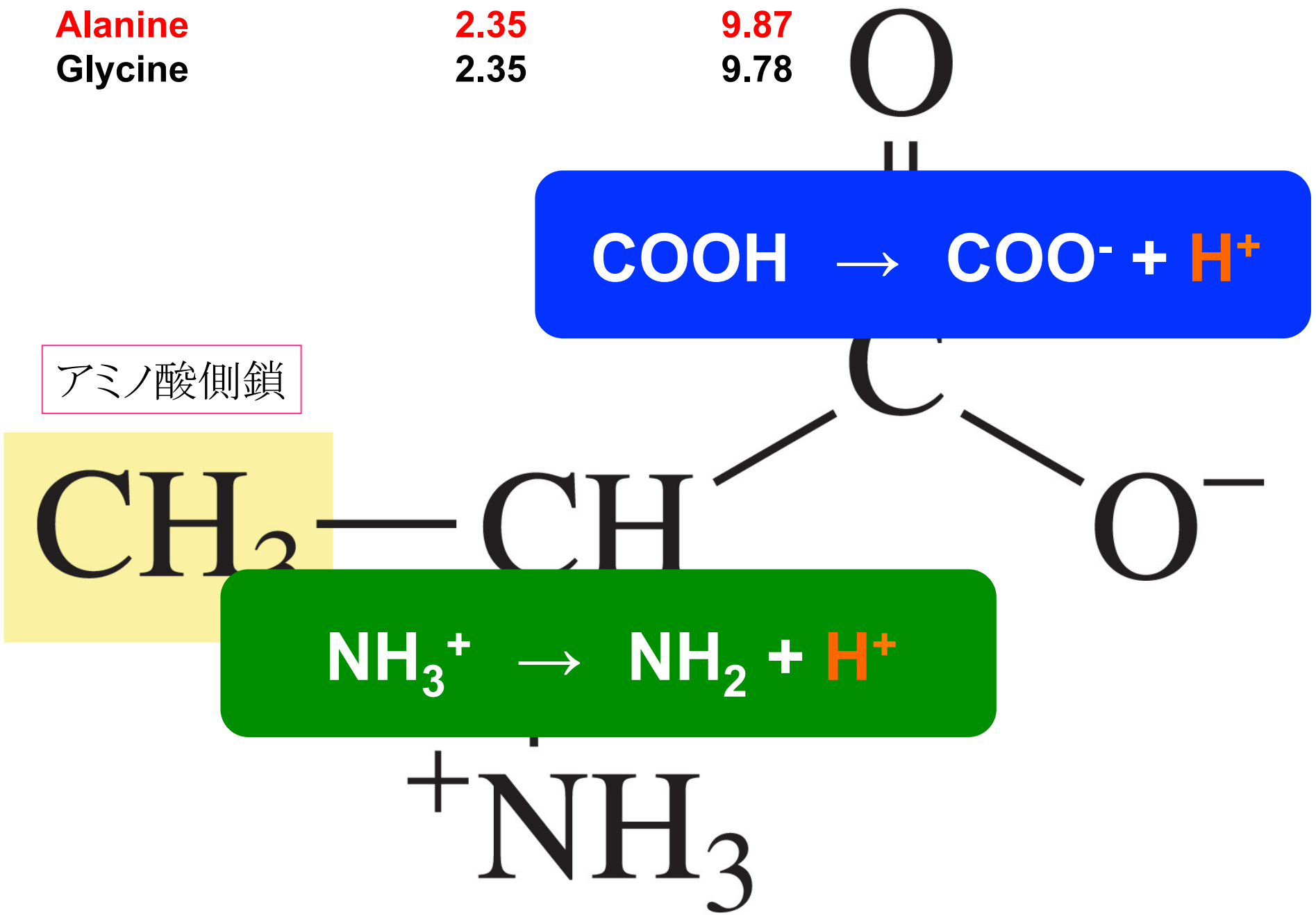
	pK_a
CH_3COOH	4.8
$ClCH_2COOH$	2.8
$ClCH_2CH_2COOH$	4.1
$ClCH_2CH_2CH_2COOH$	4.5
$ClCH_2CH_2CH_2CH_2COOH$	4.7
$Cl_2CHCOOH$	1.3
Cl_3CCOOH	0.7
FCH_2COOH	2.6



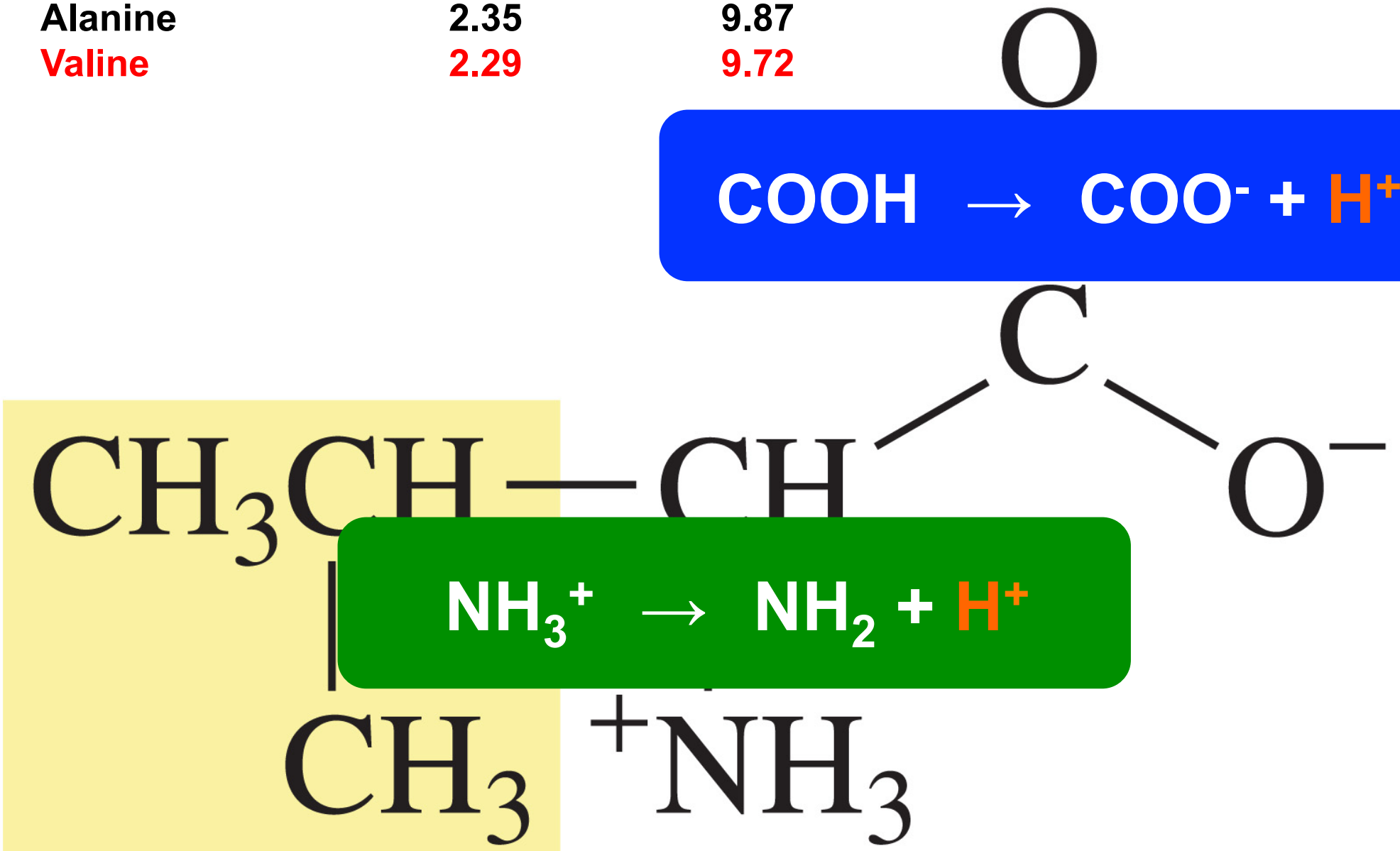
Amino Acid	α-COOH	α-NH_2	Side chain
Glycine	pK_{a1} = 2.35	pK_{a2} = 9.78	



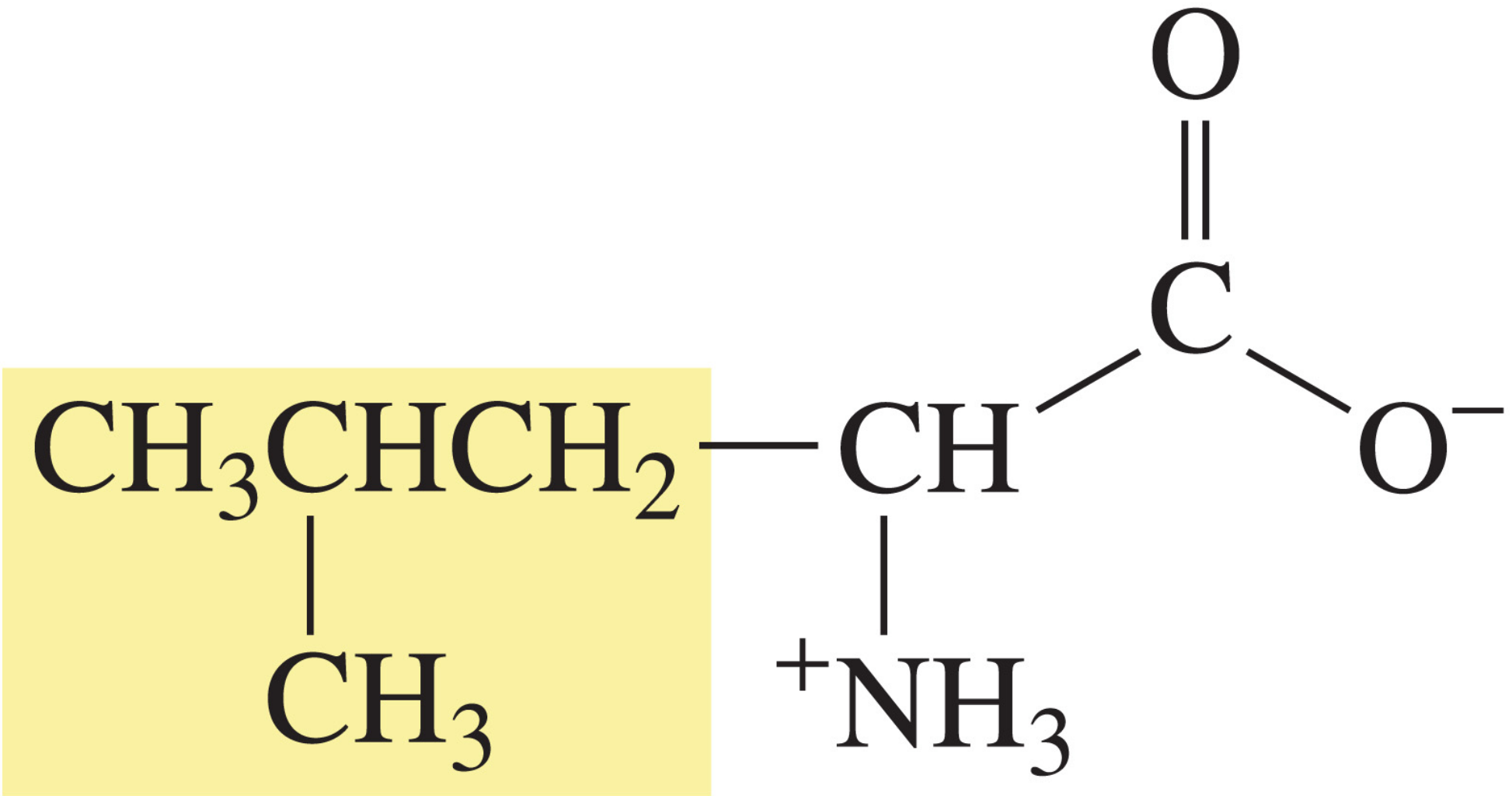
Amino Acid	α-COOH	α-NH_2	Side chain
Alanine	2.35	9.87	
Glycine	2.35	9.78	



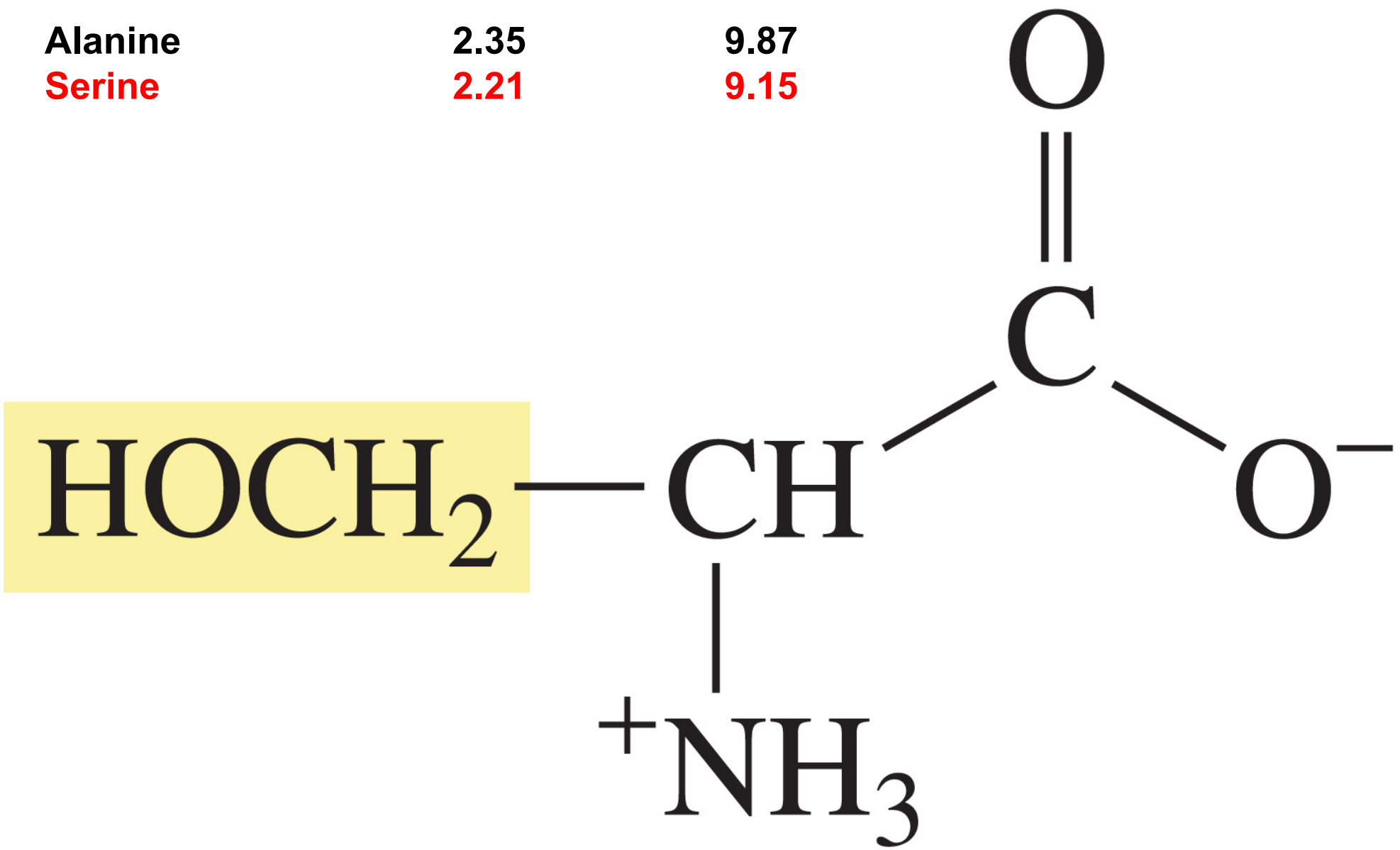
Amino Acid	α-COOH	α-NH_2	Side chain
Alanine	2.35	9.87	
Valine	2.29	9.72	



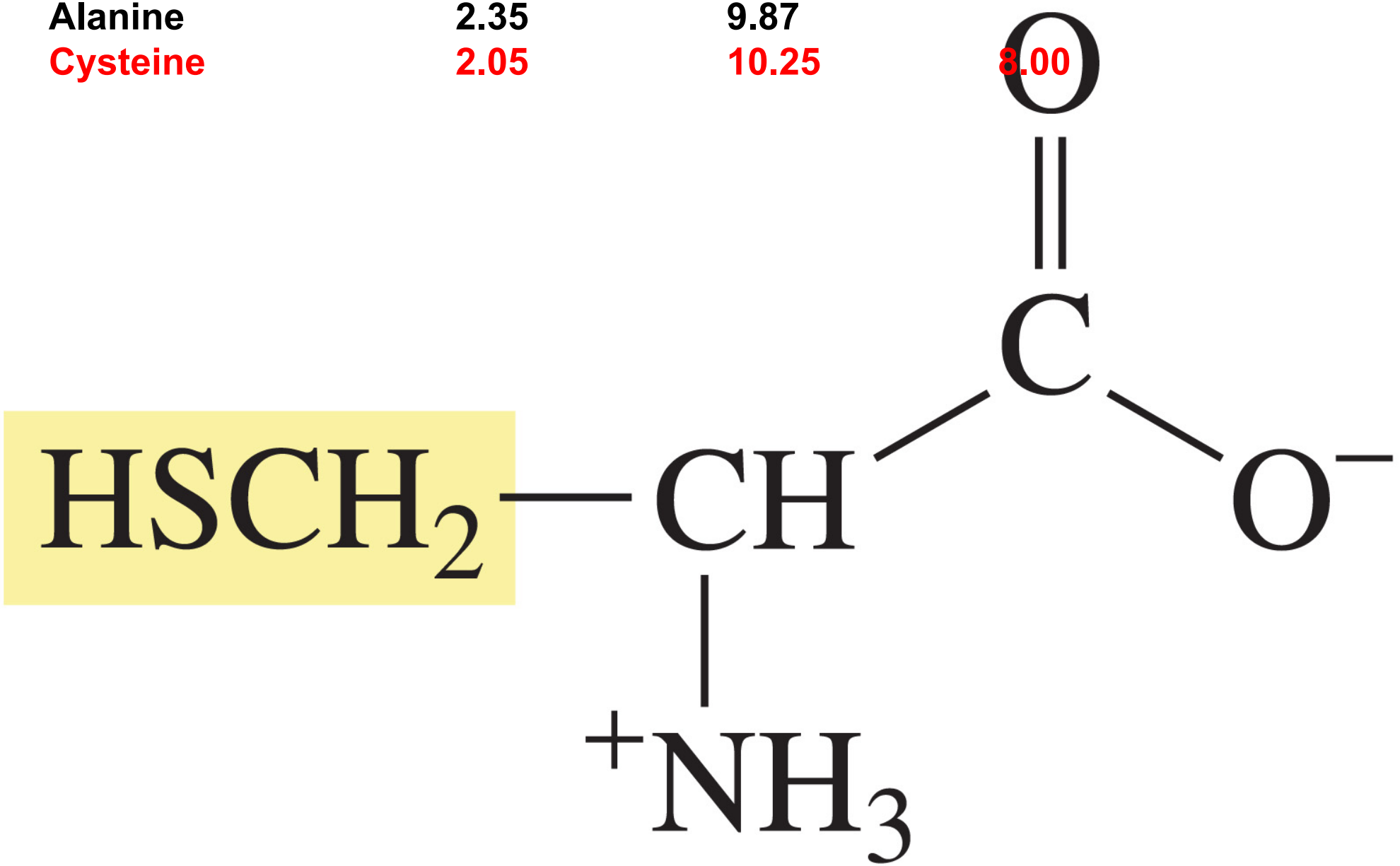
Amino Acid	α-COOH	α-NH_2	Side chain
Valine	2.29	9.72	
Leucine	2.33	9.74	



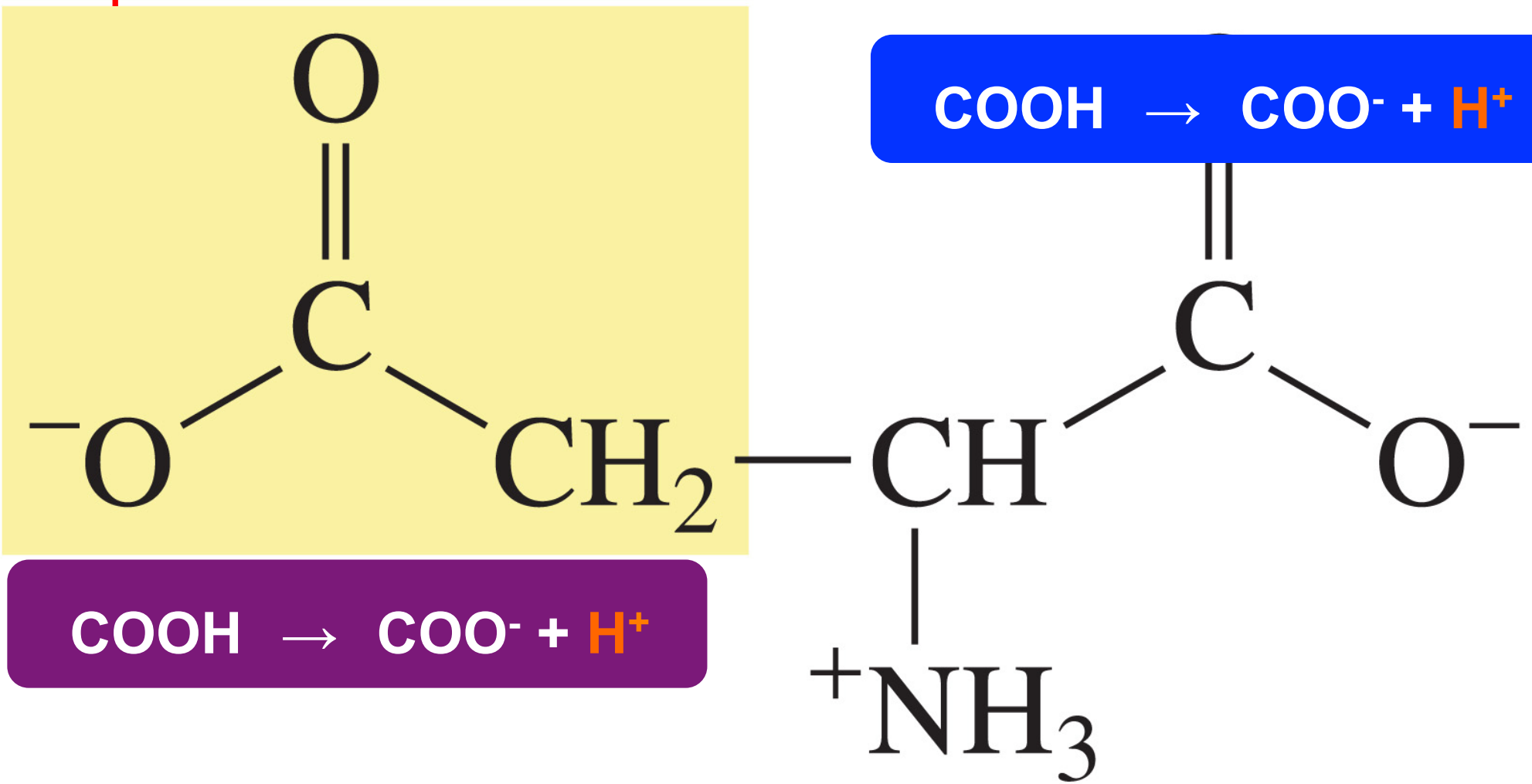
Amino Acid	α-COOH	α-NH_2	Side chain
Alanine	2.35	9.87	
Serine	2.21	9.15	



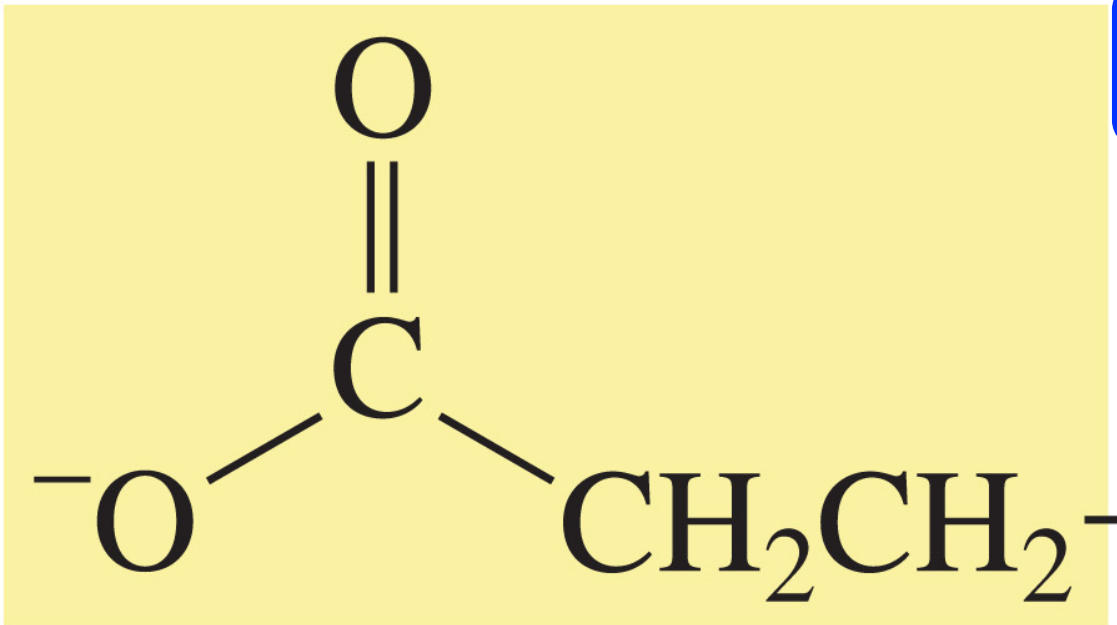
Amino Acid	α-COOH	α-NH_2	Side chain
Alanine	2.35	9.87	
Cysteine	2.05	10.25	8.00



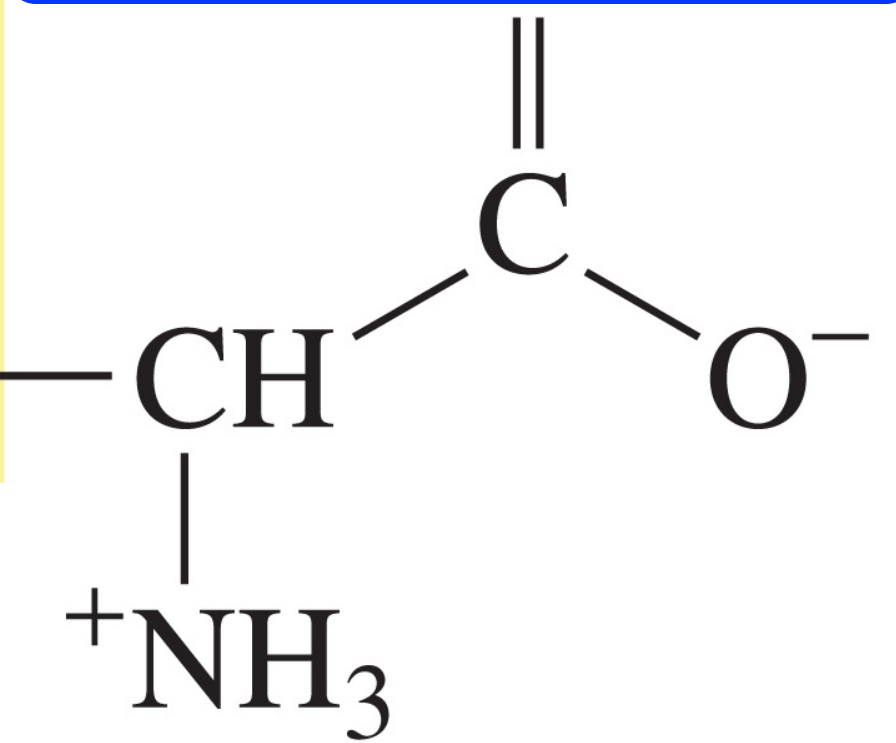
Amino Acid	α-COOH	α-NH_2	Side chain
Alanine	2.35	9.87	
Aspartic Acid	2.10	9.82	3.86



Amino Acid	α-COOH	α-NH_2	Side chain
Aspartic Acid	2.10	9.82	3.86
Glutamic Acid	2.10	9.47	4.07



$COOH \rightarrow COO^- + H^+$

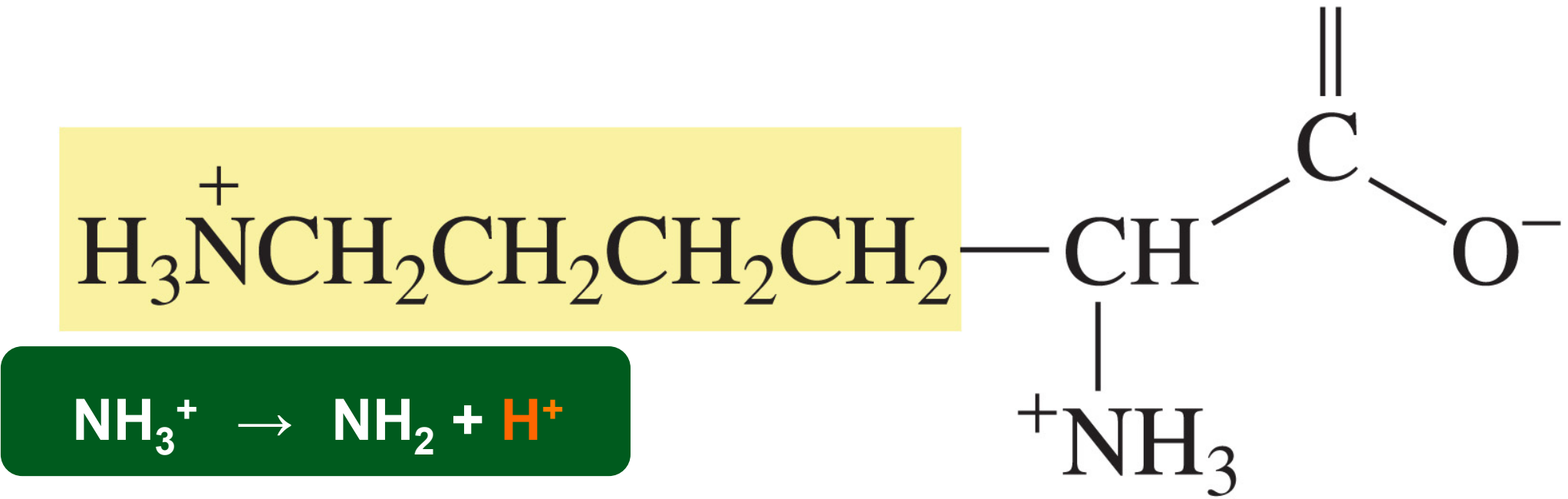


$COOH \rightarrow COO^- + H^+$

$NH_3^+ \rightarrow NH_2 + H^+$

Amino Acid	α-COOH	α-NH_2	Side chain
Glutamic Acid	2.10	9.47	4.07
Lysine	2.18	8.95	10.53

$COOH \rightarrow COO^- + H^+$



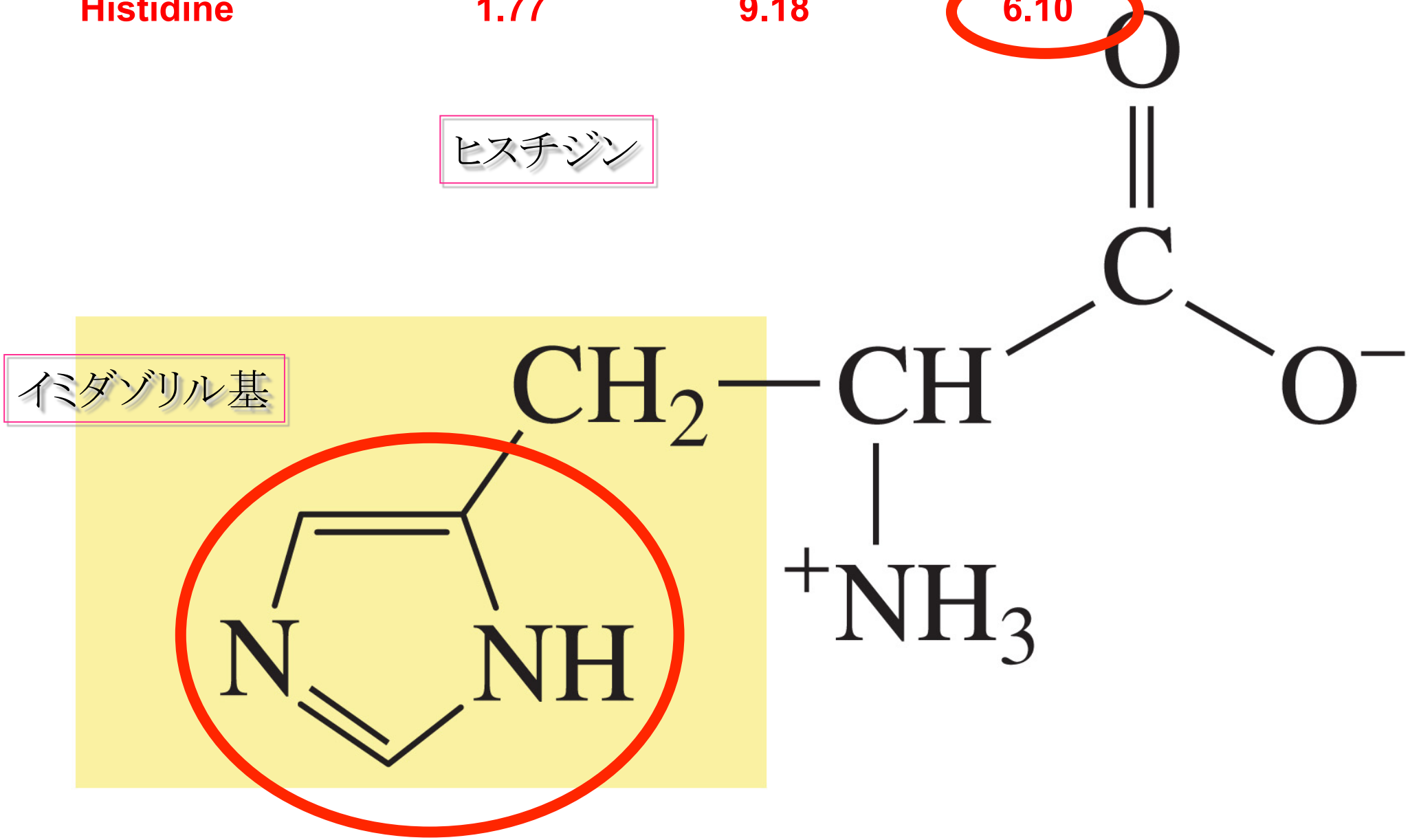
$NH_3^+ \rightarrow NH_2 + H^+$

$NH_3^+ \rightarrow NH_2 + H^+$

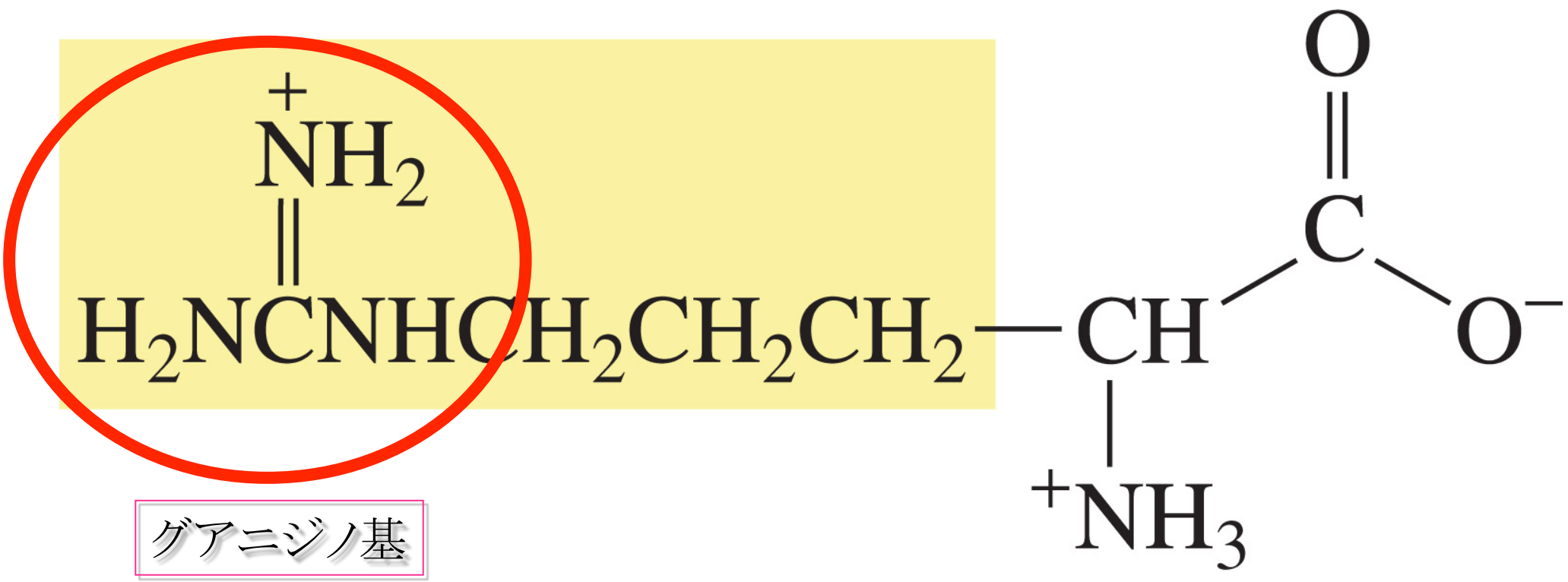
Amino Acid	α-COOH	α-NH_2	Side chain
Lysine	2.18	8.95	10.53
Histidine	1.77	9.18	6.10

ヒスチジン

イミダゾリル基

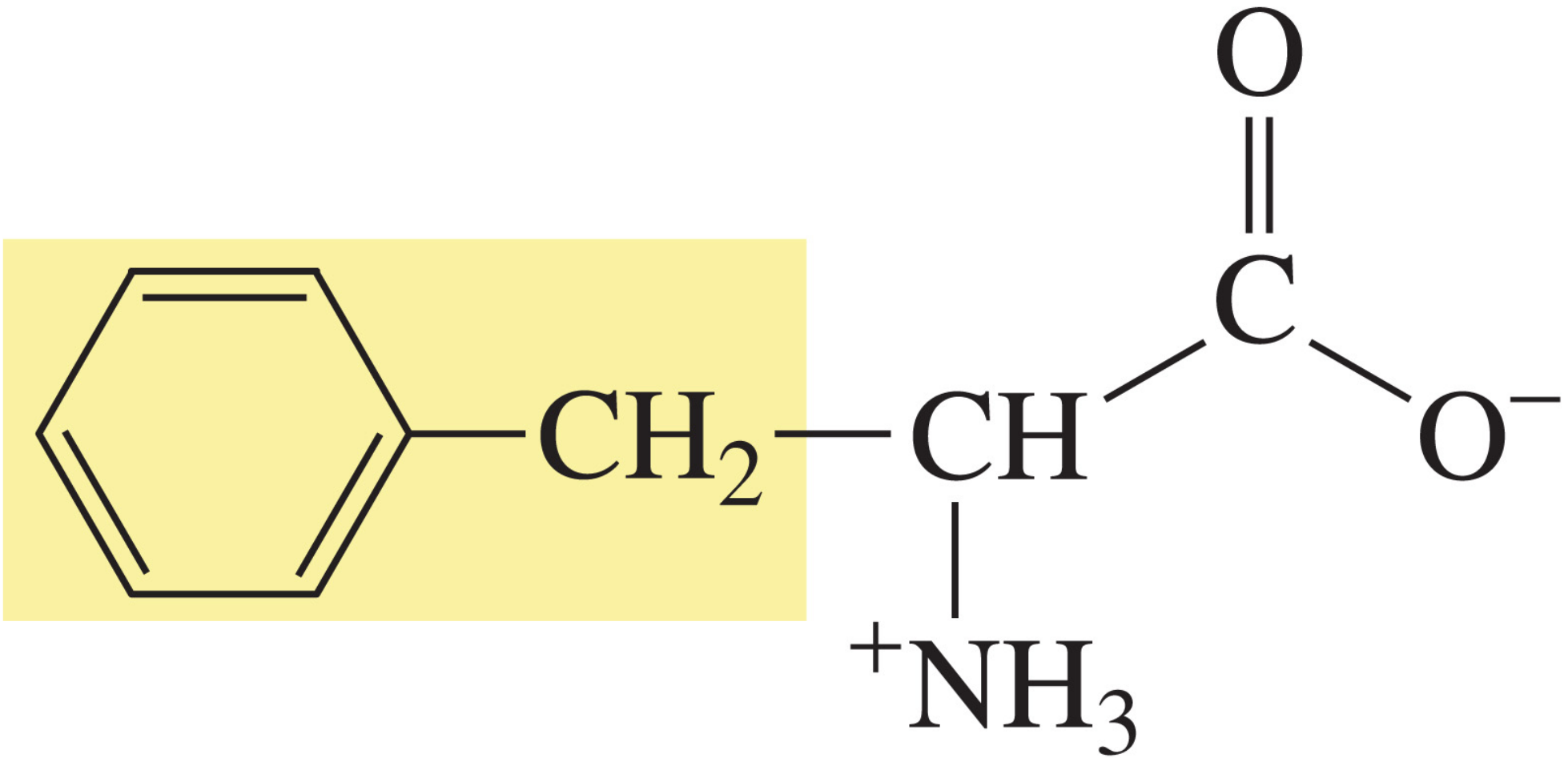


Amino Acid	α-COOH	α-NH_2	Side chain
Arginine	2.01	9.04	12.48
Histidine	1.77	9.18	6.10
Lysine	2.18	8.95	10.53

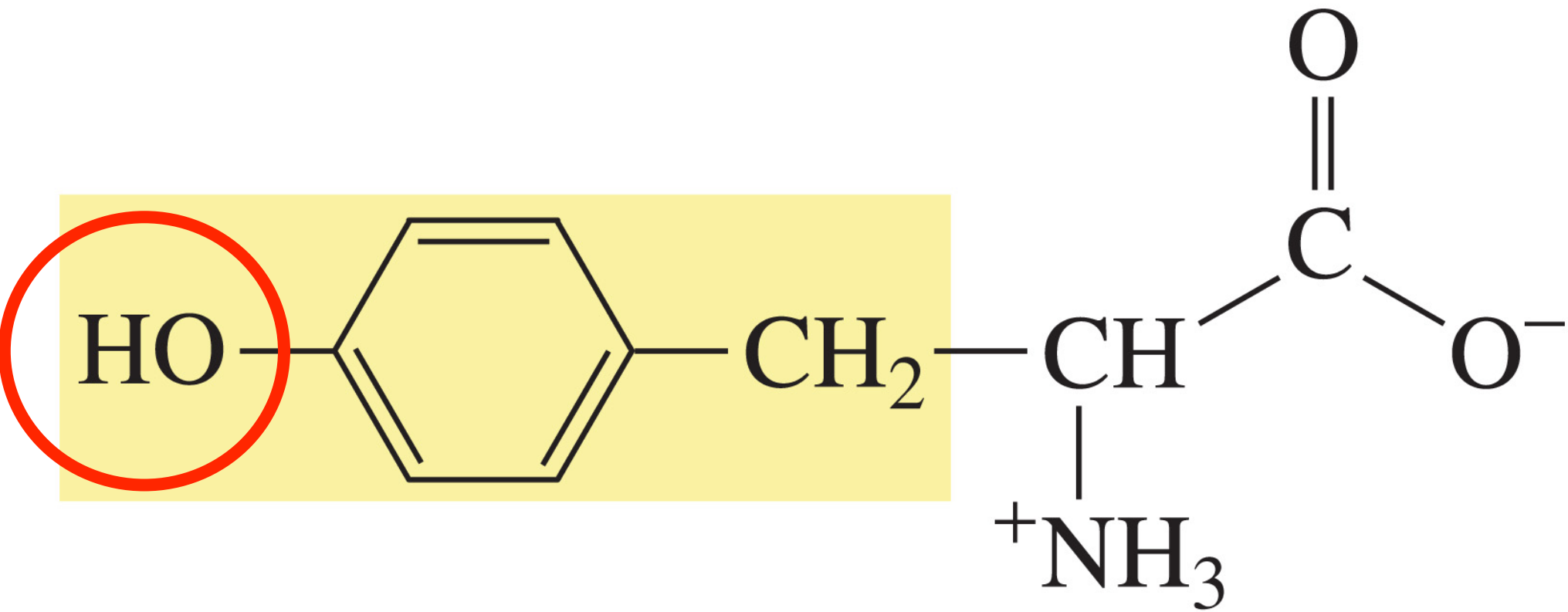


グアニジノ基

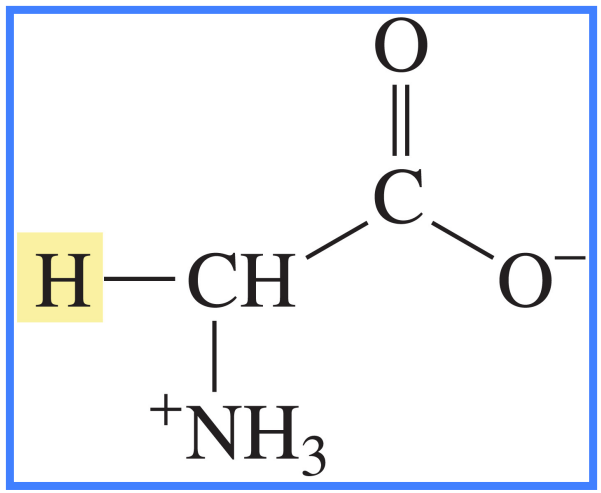
Amino Acid	α-COOH	α-NH_2	Side chain
Alanine	2.35	9.87	
Phenylalanine	2.58	9.24	



Amino Acid	α-COOH	α-NH_2	Side chain
Phenylalanine	2.58	9.24	
Tyrosine	2.20	9.11	10.07

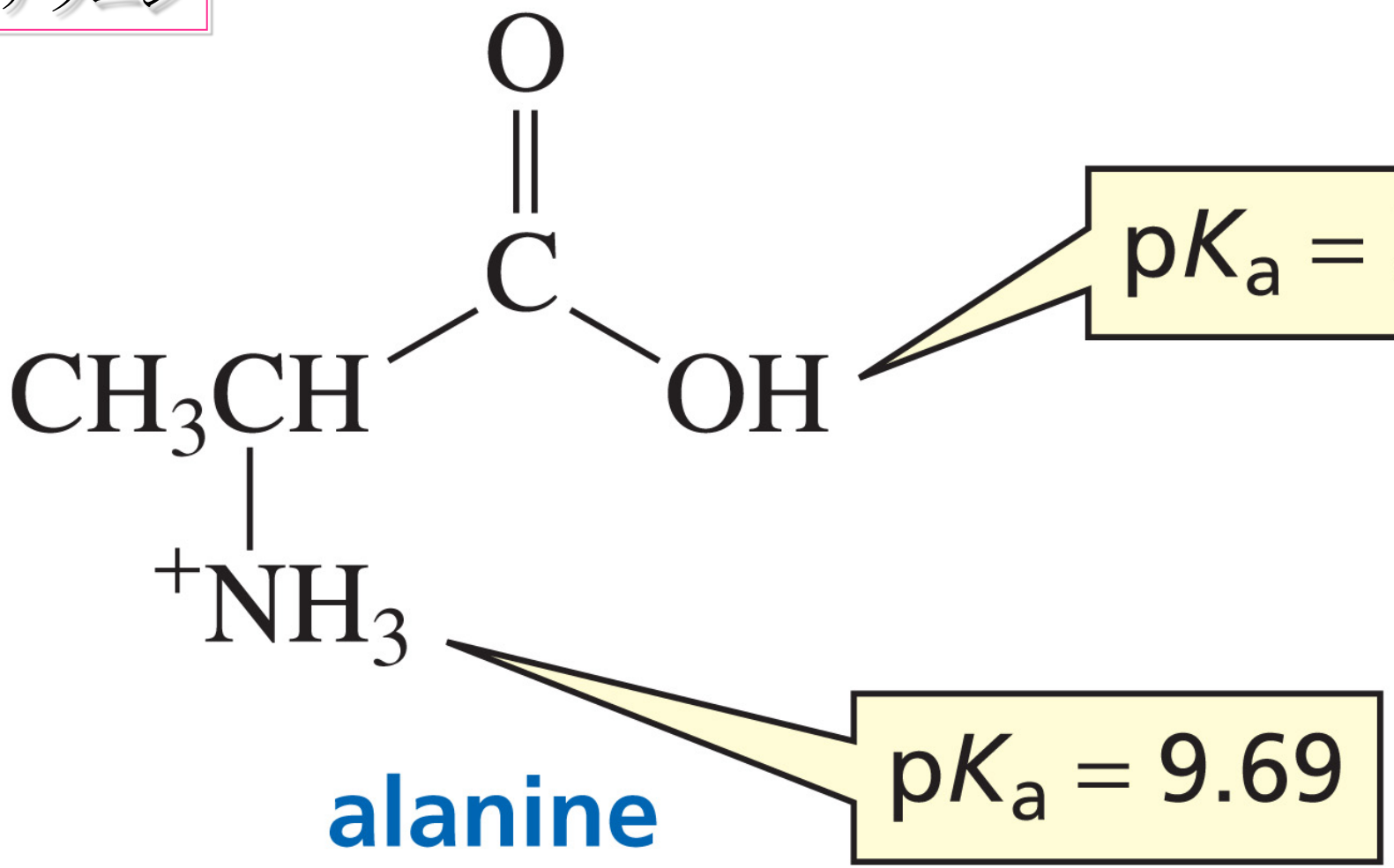


等電点（pI、Isoelectric point）



アニオンになる官能基と
カチオンになる官能基の
両方をもつ化合物において、
電離後の化合物全体の
電荷平均が0となるpHのこと。

アラニン

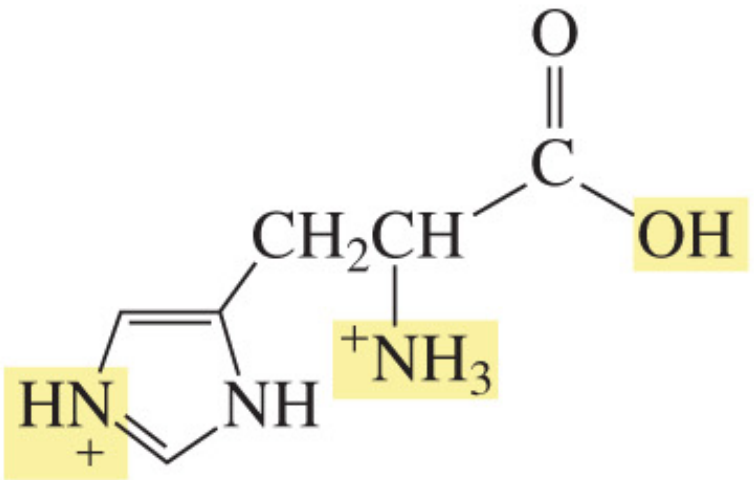


等電点

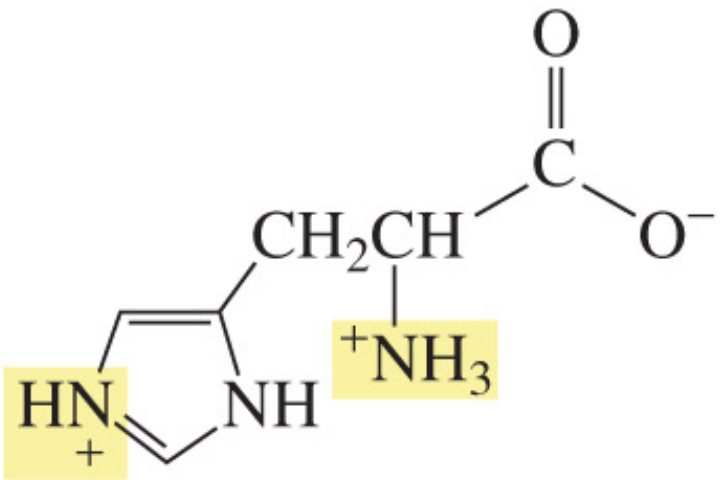
$$pI = \frac{2.34 + 9.69}{2} = \frac{12.03}{2} = 6.02$$

ヒスチジンの解離状態

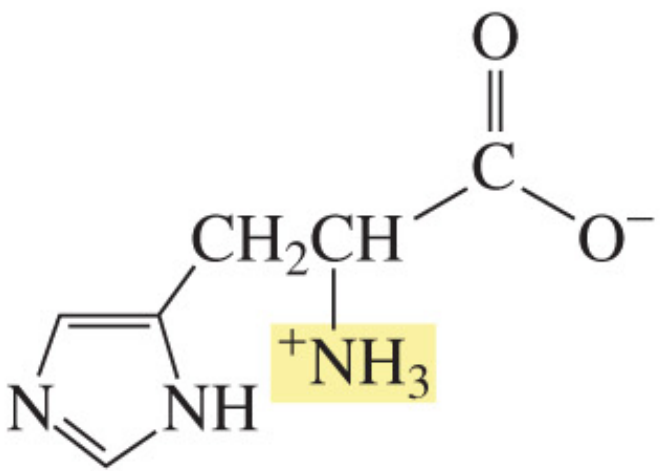
pK_1=1.77, pK_2=6.10, pK_3=9.18



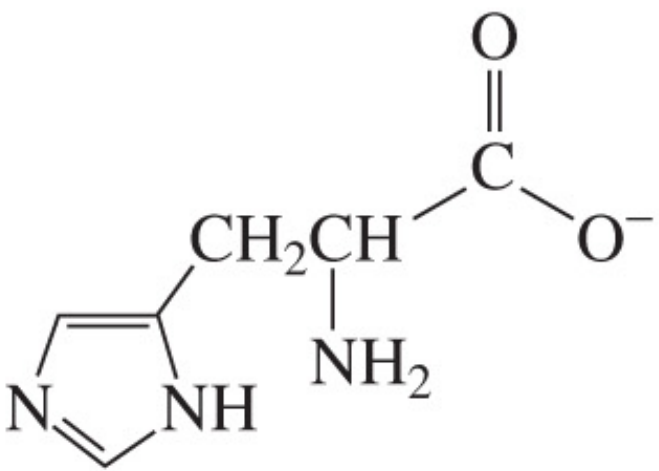
pH = 0



pH = 4



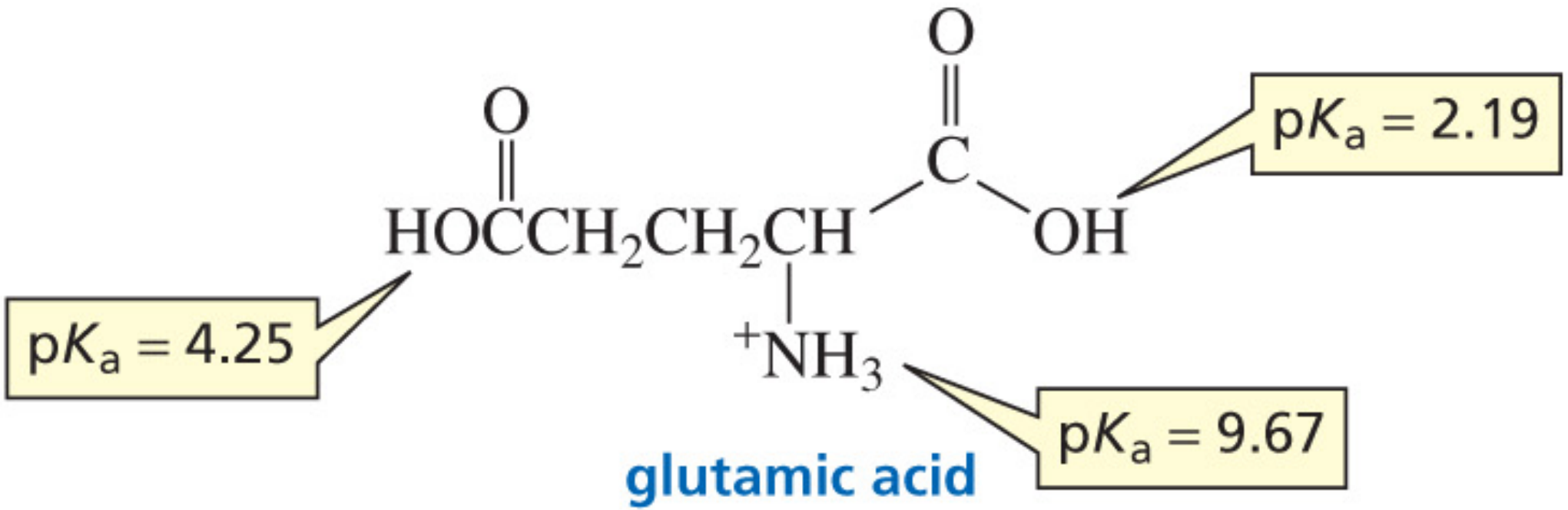
pH = 8



pH = 12

等電点

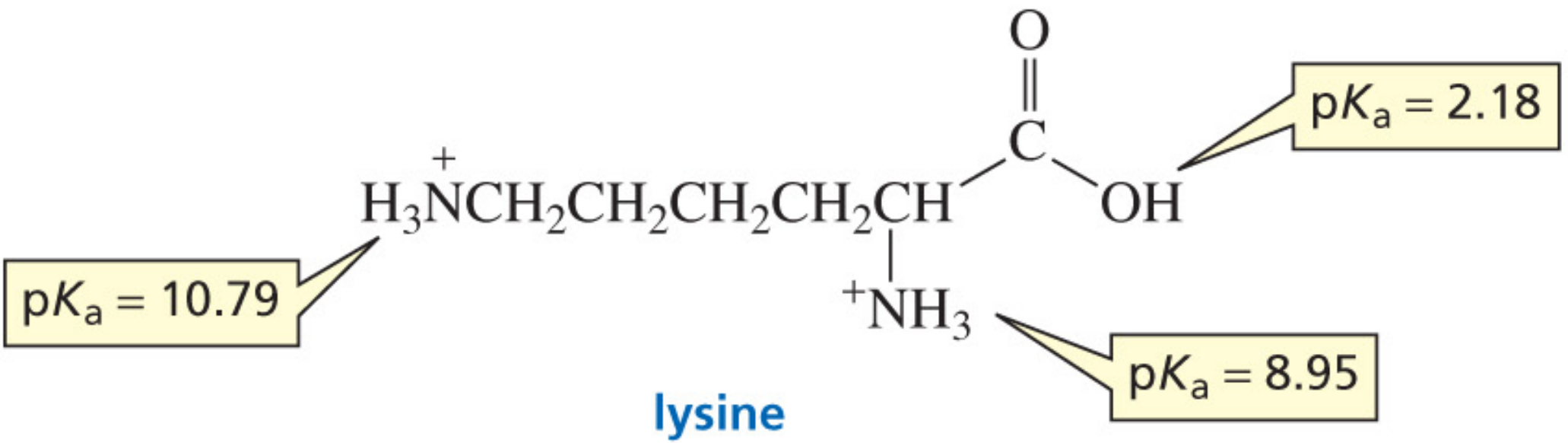
グルタミン酸



$$\mathrm{pI} = \frac{2.19 + 4.25}{2} = \frac{6.44}{2} = 3.22$$

等電点

リシン



lysine

$$\mathrm{pI} = \frac{8.95 + 10.79}{2} = \frac{19.74}{2} = 9.87$$