THE CANADIAN CHEMISTRY CONTEST 2010

for high school and CEGEP students
(formerly the National High School Chemistry Examination)

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2010

Free Response Development Problems (90 minutes)

This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 1.5 hours, it is recognized that backgrounds will vary and students will not be eliminated from further competition because they have missed parts of the paper.

Your answers are to be written in the spaces provided on this paper. All of the paper, including this cover page, along with a photocopy of Part A of the examination, is to be returned promptly to your Canadian Chemistry Olympiad Coordinator.

— PLEASE READ —

1. BE SURE TO COMPLETE THE INFORMATION REQUESTED AT THE BOTTOM OF THIS PAGE BEFORE BEGINNING PART C OF THE EXAMINATION.
2. STUDENTS ARE EXPECTED TO ATTEMPT ALL QUESTIONS OF **PART A** AND **PART C**. CREDITABLE WORK ON A LIMITED NUMBER OF THE QUESTIONS MAY BE SUFFICIENT TO EARN AN INVITATION TO THE NEXT LEVEL OF THE SELECTION PROCESS.
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.
4. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.
5. NOTE THAT A PERIODIC TABLE AND A LIST OF SOME PHYSICAL CONSTANTS WHICH MAY BE USEFUL CAN BE FOUND ON DATA SHEETS PROVIDED AT THE END OF THIS EXAMINATION.

PART A ( )
Correct Answers

25 x 1.6 = .../040

PART C

1. ..../012
2. ..../012
3. ..../012
4. ..../012
5. ..../012

TOTAL ..../100

Name ______________________ (LAST NAME, Given Name; Print Clearly) School ______________________

City ______________________ Province ______________________

Date of birth ______________________ E-Mail ______________________

Home Telephone ( ) - ______________________ Years at a Canadian high school ___

Number of chemistry courses at a Québec CÉGEP ___

Male ❒ Canadian Citizen ❒ Landed Immigrant ❒ Visa Student ❒

Female ❒ Passport valid until November 2010 ❒

Nationality of Passport ______________________

INORGANIC CHEMISTRY

1. In 1899, Ludwig Mond reported that the complex $Ni(CO)_4$ could be obtained directly by passing a flow of carbon monoxide over impure nickel. Remarkably, the boiling point of this complex is 43^{o}C, which makes it one of the most volatile metal complexes known. Lord Kelvin (of temperature unit fame) said that Mond had "given wings to heavy metals". This unique property facilitates isolation of very pure nickel by distillation of the complex, followed by heating at a temperature over 180^{o}C to remove carbon monoxide. However, the complex is highly toxic and great care must be taken while handling it.

(a). What is the oxidation state of nickel in the complex $Ni(CO)_4$?

1 mark

(b). Draw the best structure for carbon monoxide that obeys the octet rule around both the C and the O atom. Clearly include all lone pairs of electrons and formal charges if appropriate.

4 marks

(c). What is the coordination geometry of the Ni atom in $Ni(CO)_4$?

1 mark

(d). Heating nickel(II) oxide with molecular hydrogen at 200^{o}C yields metallic nickel. Write a balanced equation for this reaction, including the state of matter for all reactants and products.

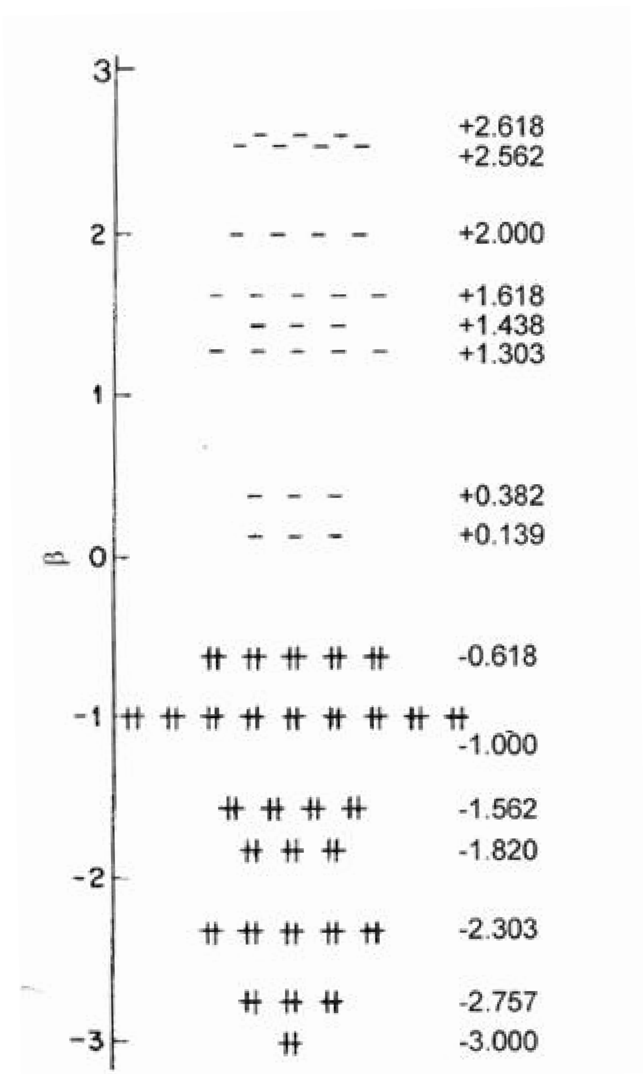
4 marks

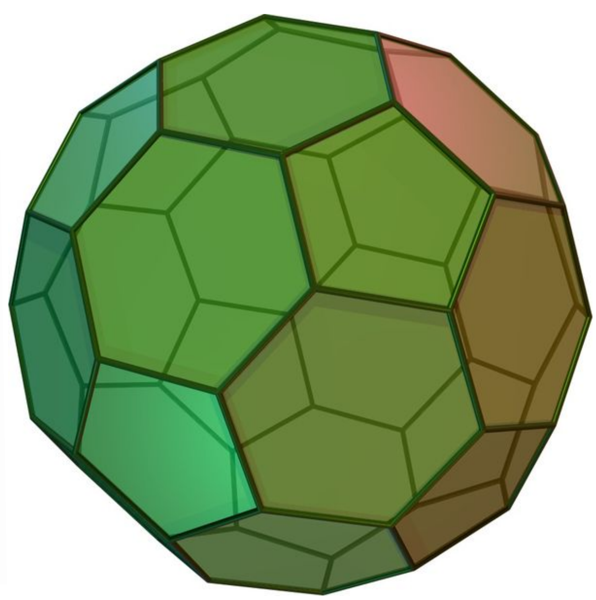
(e). The stability of $Ni(CO)_4$ can be in part explained by the saturation of the valence shell of nickel. Knowing this, what formula would you expect for the corresponding iron carbonyl complex? Briefly explain your answer.

2 marks

2. Fullerenes are a family of megamolecules comprised entirely of carbon atoms that take various three-dimensional forms, including spheres, tubes, and planes. Much current research revolves around their potential nanotechnology applications: carbon nanotubes, for example, are being examined for their utility as both biomedical and electronic sensors.

Discovered by Sir Harry Kroto and his collaborators in 1985, C_{60} (also known as buckminsterfullerene) was the first fullerene ever isolated. Buckminsterfullerene takes the shape of a truncated icosahedron, or in more familiar terms, a soccer ball – each vertex of a soccer ball is replaced by a carbon atom. Buckminsterfullerene contains a network of π-electrons that tries to delocalize throughout the ball. Unlike benzene, it is *not* a truly aromatic molecule, although it exhibits various aromatic properties. A molecular orbital diagram of buckminsterfullerene is shown below; the energies are in units of β.





(a). Is ground-state buckminsterfullerene diamagnetic? (circle the correct response).

Yes No

0.5 marks

(b). Based on your above answer, would buckminsterfullerene be attracted to or repelled by an external magnetic field? (circle the correct response).

Attracted Repelled

0.5 marks

(c).How many bonding and antibonding orbitals are found in ground-state buckminsterfullerene? How many of each are occupied?

	Total orbitals	Occupied orbitals
Bonding		
Antibonding		

2 marks

(d). How many ^{13}C NMR signals would be observed for buckminsterfullerene? In other words, how many structurally-different environments do carbon atoms find themselves in?

1 mark

(e). Name the two most common forms of elemental carbon (allotropes) and the hybridization of the carbon atoms in each form.

Form of elemental carbon	Hybridization

2 marks

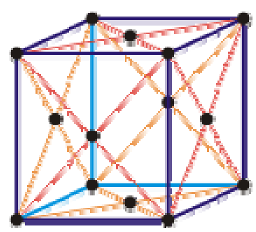
(f). A mass spectrometric analysis of buckminsterfullerene measures the m/z mass-to-charge ratio of ionized C_{60}^{+}. The three largest peaks are observed at m/z = 720, 721, and 722. Determine the theoretical ratio of the three m/z peaks mentioned above. The proportion of the m/z = 720 peak is pre-normalized to 100.

Isotope	Natural abundance
^{12}C	98.89 %
^{13}C	1.11 %
^{14}C	negligible

m/z ratio	Relative proportion
720	100
721	
722	

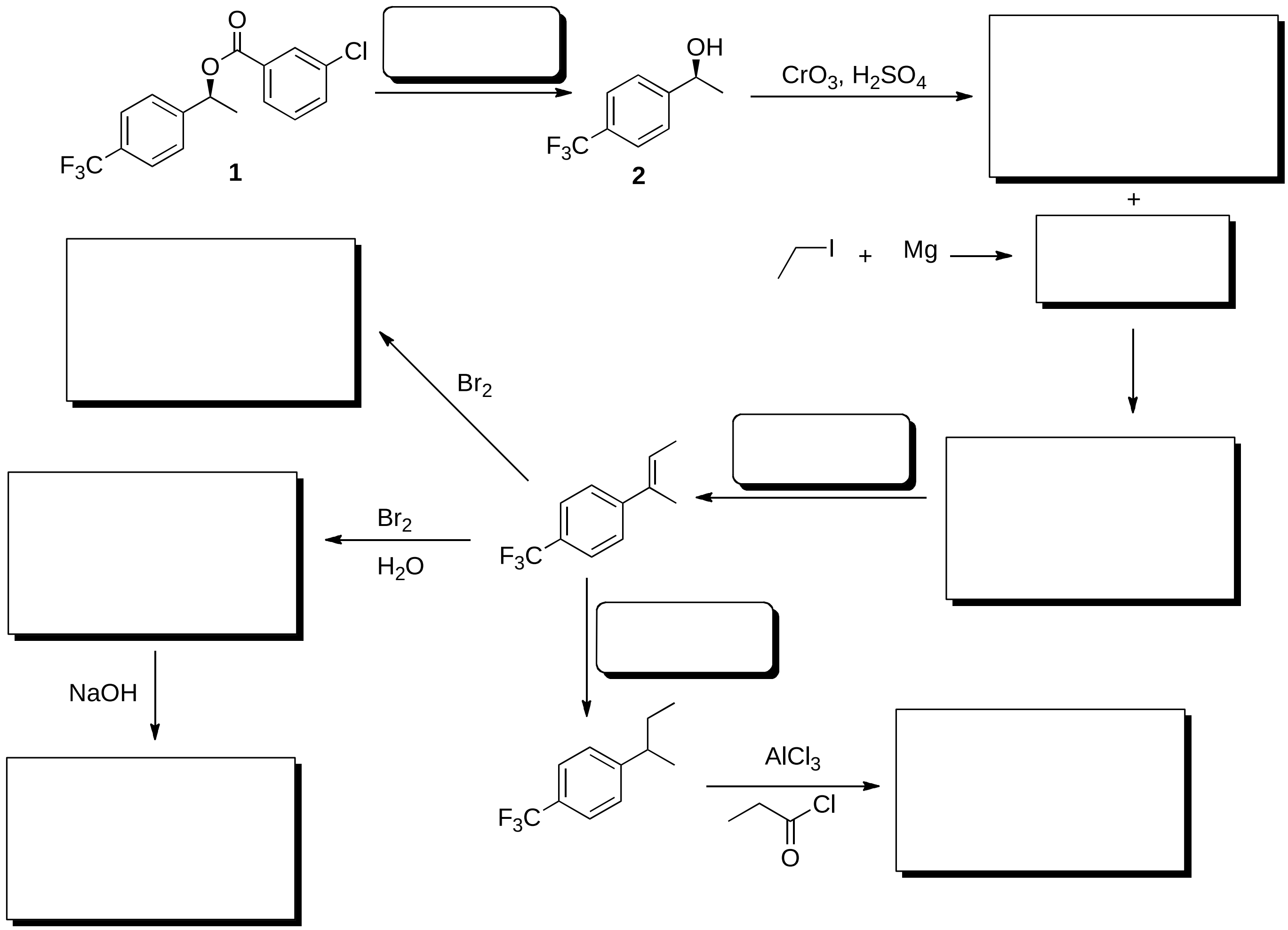
2 marks

(g). Fullerenes can be doped with alkali metals to form superconductors. The fullerenes form a face-centred cubic structure – in other words, the C_{60}^{x-} anions are located at both the vertices and the centres of the faces of the unit cell (shown below). The small alkali metal ions are located in the tetrahedral and octahedral holes. The radius of a fullerene anion is 4.98 Å. The density of one of the first such superconductors, prepared with potassium, is 1.987 g/cm^3. Showing all working, determine the formula of K_xC_{60}.



4 marks

3. Consider the reaction scheme below.



(a). In the reaction scheme, compound **1** is converted to compound **2** under a particular set of conditions. Redraw compound **1** below and circle and name the functional group that reacts when **1** is converted to **2**.

1 mark

(b). What is the molecular formula of compound **1**?

1 mark

(c). In the reaction scheme, complete each box to show either the major product of the reaction or a reasonable set of reaction conditions to achieve the shown transformation. Show relative stereochemistry where appropriate.

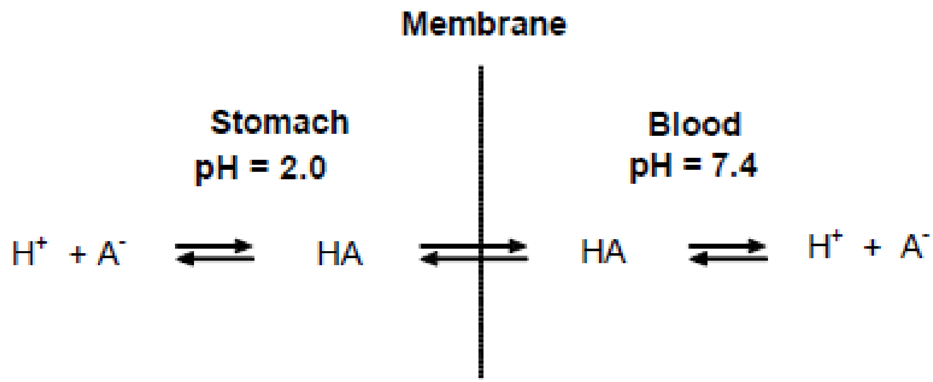
10 marks

4. This question is about determining base and acid concentrations under different conditions.

(a). Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm^3 aqueous solution containing 3.48 cm^3 of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. State the answer to three significant figures. For aqueous H_3PO_4: purity = 85% by mass, density = 1.69 g/cm^3, pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.44.

6 marks

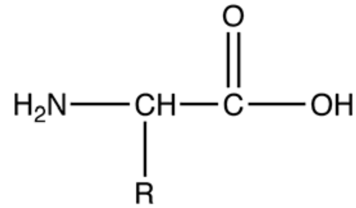
(b). The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Calculate the ratio of the total concentration of aspirin (acetylsalicylic acid, pK_a = 3.52, [HA] + [A^-]) in the blood to that in the stomach. Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides.

6 marks

5. An amino acid is one of the fundamental molecules found in living organisms. A general structure of an amino acid is given below. R denotes a side chain group of some kind (see attached data sheet).



(a). In an amino acid, the pK_a of the amino group is about 10 while the pK_a of the carboxylic acid group is about 3. Assuming there is no charge at the side chain (R) group, state the net charge on the molecule under the following conditions:

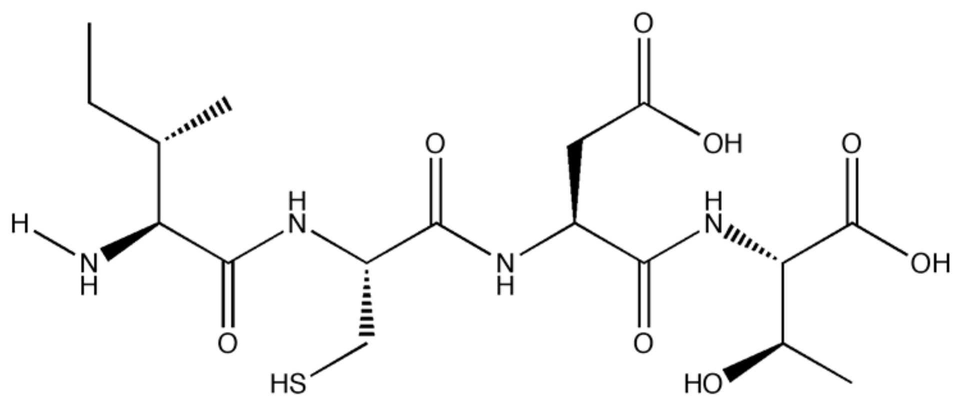
(i). pH = 7.0

(ii). pH = 2.0

(iii). pH = 11.0

1.5 marks

(b). Amino acids can form chain-like structures called peptides through so-called "peptide linkages". An example of a peptide is given below.



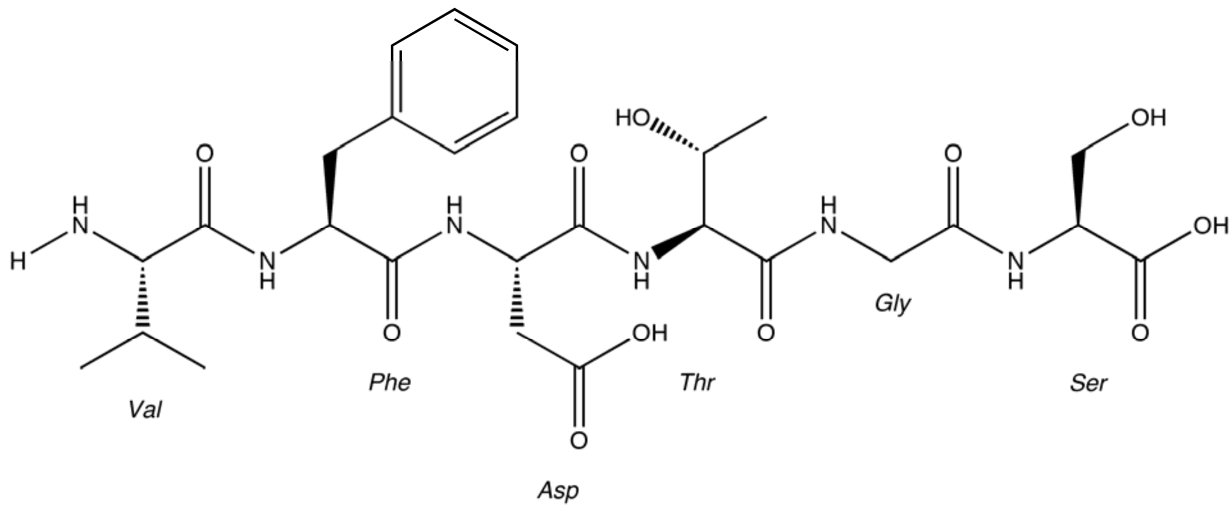
(c). Write a general chemical equation to show peptide bond formation from two amino acids. Simplify each amino acid as $H_2NCHRCOOH$.

3 marks

(d). Write the amino acid sequence of the peptide given above (hint: identify the amino acid side chain groups and find the appropriate three letter codes (e.g. "Gly" for glycine) on the attached data sheet).

2 marks

(e). In the stomach, two types of cells work together to help the digestion of dietary proteins. Firstly, chief cells secrete pepsinogen that is activated in an acidic environment into the enzyme pepsin, which digests food peptides. Secondly, parietal cells secrete protons via potassium-transporting ATPase (also called a *proton pump*) to regulate the pH of the stomach. The following is a partial sequence of the active site of pepsin (see attached data sheet for the amino acid three letter codes and side chain pK_a values).



(i). What is the net charge of this partial peptide at pH = 1.5?

1 mark

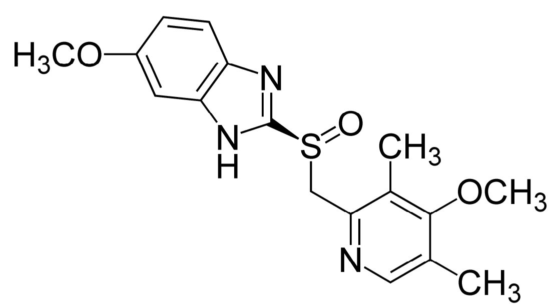
(ii). What is the net charge of this partial peptide at pH = 5.0?

1 mark

(iii). Briefly explain why pepsin becomes inactive at pH = 5.0.

1.5 marks

(f). Excessive acid production in the stomach irritates the stomach lining and causes many problems including ulcers. A way to treat this condition is to block the action of the proton pump. Below is the structure of a drug (omeprazole) that inhibits the action of the proton pump.



The drug is inactive in this form until it is activated by the acid in the stomach. On the above structure, circle all the atoms that could act as a proton acceptor during the activation.

2 marks

--END OF PART C--

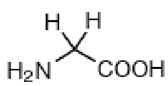
Data Sheet

Physical Constants

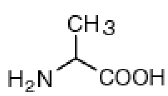
Name	Symbol	Value
Avogadro's constant	N_A	6.0221×10^{23} mol^{-1}
Boltzmann constant	k_B	1.3807×10^{-23} J K^{-1}
Gas constant	R	8.3145 J K^{-1} mol^{-1}
Faraday constant	F	96485 C mol^{-1}
Speed of light	c	2.9979×10^{8} m s^{-1}
Planck's constant	h	6.6261×10^{-34} J s
Standard pressure	$p°$	10^5 Pa
Atmospheric pressure	p_{atm}	1.01325×10^5 Pa
Zero of the Celsius scale		273.15 K

Amino Acids

Small

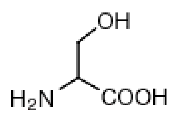


Glycine (Gly, G)
MW: 57.05

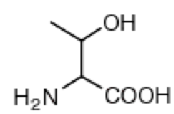


Alanine (Ala, A)
MW: 71.09

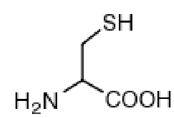
Nucleophilic



Serine (Ser, S)
MW: 87.08, pK_a ~ 16

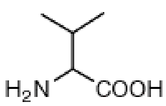


Threonine (Thr, T)
MW: 101.11, pK_a ~ 16

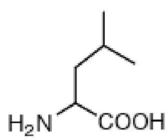


Cysteine (Cys, C)
MW: 103.15, pK_a = 8.35

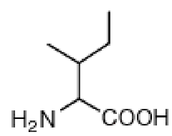
Hydrophobic



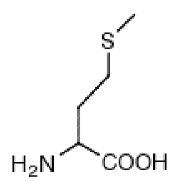
Valine (Val, V)
MW: 99.14



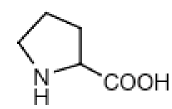
Leucine (Leu, L)
MW: 113.16



Isoleucine (Ile, I)
MW: 113.16

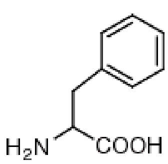


Methionine (Met, M)
MW: 131.19

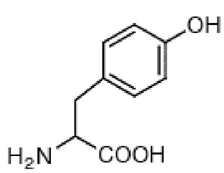


Proline (Pro, P)
MW: 97.12

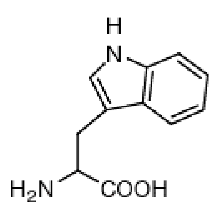
Aromatic



Phenylalanine (Phe, F)
MW: 147.18

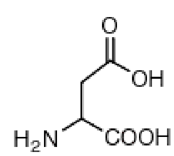


Tyrosine (Tyr, Y)
MW: 163.18

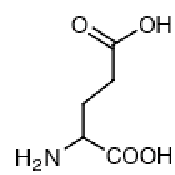


Tryptophan (Trp, W)
MW: 186.21

Acidic

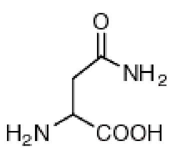


Aspartic Acid (Asp, D)
MW: 115.09, pK_a = 3.9

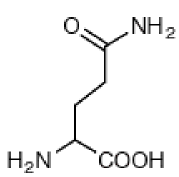


Glutamic Acid (Glu, E)
MW: 129.12, pK_a = 4.07

Amide

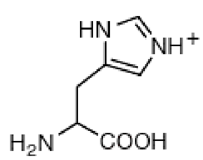


Asparagine (Asn, N)
MW: 114.11

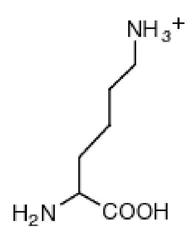


Glutamine (Gln, Q)
MW: 128.14

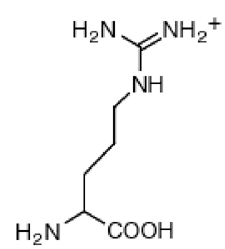
Basic



Histidine (His, H)
MW: 137.14, pK_a = 6.04



Lysine (Lys, K)
MW: 128.17, pK_a = 10.79



Arginine (Arg, R)
MW: 156.19, pK_a = 12.48

Data Sheet
Fiche de données

Relative Atomic Masses (1985 IUPAC)
*For the radioactive elements the atomic mass of an important isotope is given

Masses Atomiques Relatives (UICPA,1985)
*Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.07	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs	109 Mt	110 Ds								

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
90 Th 232.038	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

	Symbol Symbole	**Value Quantité numérique**	
Atomic mass unit	amu	1.66054×10^{-27} kg	Unité de masse atomique
Avogadro's number	N	6.02214×10^{23} mol^{-1}	Nombre d'Avogadro
Bohr radius	a_0	5.292×10^{-11} m	Rayon de Bohr
Boltzmann constant	k	1.38066×10^{-23} J K^{-1}	Constante de Boltzmann
Charge of an electron	e	1.60218×10^{-19} C	Charge d'un électron
Dissociation constant (H_2O)	K_w	10^{-14} (25 °C)	Constante de dissociation de l'eau (H_2O)
Faraday's constant	F	96 485 C mol^{-1}	Constante de Faraday
Gas constant	R	8.31451 J K^{-1} mol^{-1}	Constante des gaz
		0.08206 L atm K^{-1} mol^{-1}	
Mass of an electron	m_e	9.10939×10^{-31} kg	Masse d'un électron
		5.48580×10^{-4} amu	
Mass of a neutron	m_n	1.67493×10^{-27} kg	Masse d'un neutron
		1.00866 amu	
Mass of a proton	m_p	1.67262×10^{-27} kg	Masse d'un proton
		1.00728 amu	
Planck's constant	h	6.62608×10^{-34} J s	Constante de Planck
Speed of light	c	2.997925×10^{8} m s^{-1}	Vitesse de la lumière

1 Å	=	1×10^{-8} cm
1 eV	=	1.60219×10^{-19} J
1 cal	=	4.184 J
1 atm	=	101.325 kPa
1 bar	=	1×10^{5} Pa