

THE CANADIAN CHEMISTRY CONTEST 2015
for high school and CEGEP students
(formerly the National High School Chemistry Examination)

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2015

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 **IMMEDIATELY** by courier 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 A DATA SHEET 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 _____ School _____
(LAST NAME, Given Name; Print Clearly)

City & Province _____ Date of Birth _____

E-Mail _____ Home Telephone () - _____

Years at a Canadian high school ____ No. of chemistry courses at a Québec CÉGEP ____

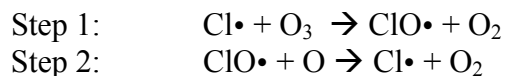
Male Canadian Citizen Landed Immigrant Visa Student

Female Passport valid until February 2016 Nationality of Passport _____

Teacher _____ Teacher E-Mail _____

PHYSICAL CHEMISTRY

1. Chlorine in the atmosphere reacts readily with ozone. One of the many reaction pathways between chlorine radicals and ozone in the troposphere occurs as follows:



(a). Write a balanced equation for the overall reaction taking place in the troposphere.

1 mark

(b). What role do Cl atoms play in the overall reaction?

1 mark

Parts (c). and (d). refer to Step 1:

In an experiment measuring the reaction between ozone and atomic chlorine, the following data were recorded at 298 K:

[Cl] (molecule cm ⁻³)	[O ₃] (molecule cm ⁻³)	Rate (molecule cm ⁻³ s ⁻¹)
4.80 x 10 ¹¹	8.22 x 10 ⁹	4.75 x 10 ¹⁰
9.60 x 10 ¹¹	1.64 x 10 ¹⁰	1.91 x 10 ¹¹
9.66 x 10 ¹¹	3.25 x 10 ¹⁰	3.79 x 10 ¹¹

(c). Write out the rate equation for this reaction.

1 mark

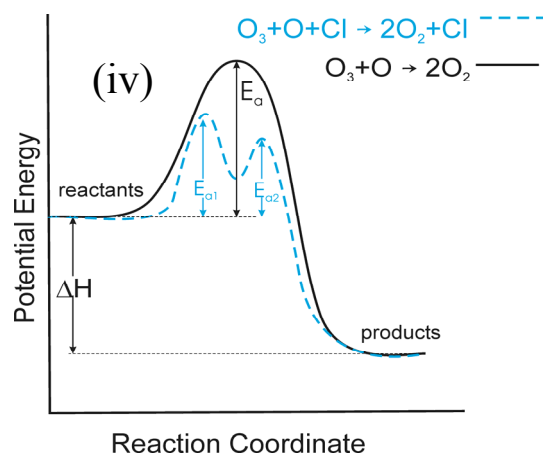
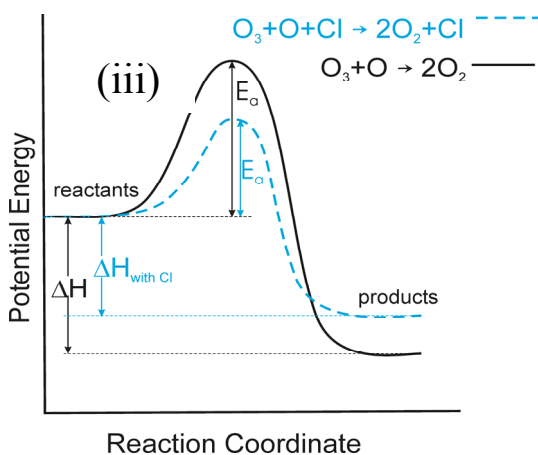
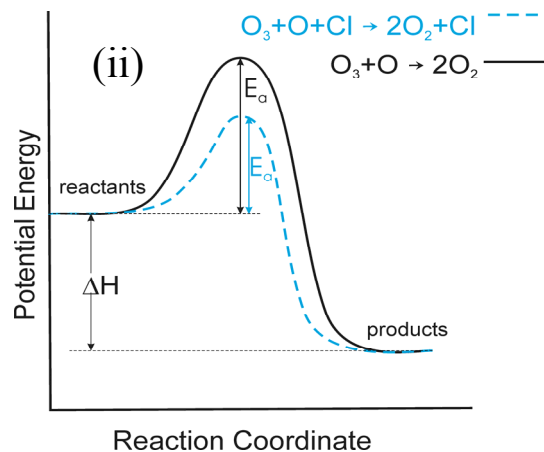
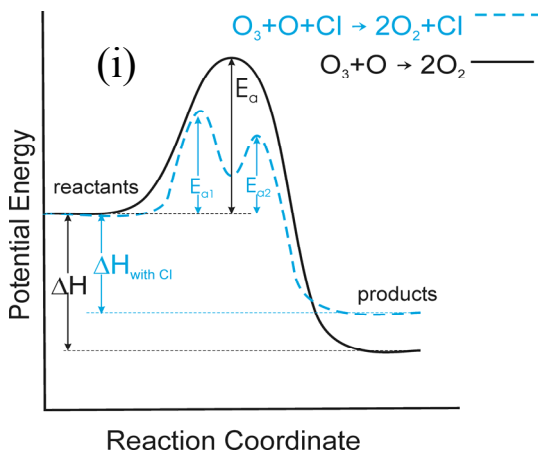
(d). Calculate the rate constant, *k* at 298K, and give its units.

1 mark

(e). At 200K, the rate constant for Step 1 is 66% of its value at 298K. Showing all work, calculate the activation energy of this reaction.

3 marks

(f). From the four reaction energy diagrams below for the breakdown of ozone by chlorine atoms, which best represents the influence of chlorine? (circle one of (i), (ii), (iii) or (iv)).



1 mark

(g). One way to measure the relative concentrations of atomic chlorine is using spectroscopic methods, where the resonant fluorescence of Cl is monitored as it reacts with ozone. This fluorescence signal arises predominantly from the $(4s^1 3p^4)^4P_{3/2} \rightarrow (3p^5)^2P_{3/2}$ transition in chlorine, with an energy difference of 9.0 eV. What wavelength of light does this transition give rise to? (the charge of one electron, $1.602 \times 10^{-19} \text{ C} = 1.0 \text{ eV}$).

1 mark

(h). Both ozone and molecular oxygen are susceptible to photolysis. Photolysis of O_2 requires a photon of no more than 240 nm, whereas photolysis of O_3 requires a photon of no more than 320 nm. Draw Lewis structures of O_2 and O_3 including resonance structures and the locations of lone pair electrons. Which molecule has stronger bonds and why?

3 marks

INORGANIC CHEMISTRY

2. Lithium ion batteries are widely used as rechargeable energy sources in smartphones, tablets and cordless power tools. Lithium ion batteries have distinct advantages over other rechargeable energy sources, such as lighter weight, smaller size and higher energy density. However, their disadvantages are well-documented: overheating lithium ion batteries caused fires that led to the world-wide grounding of all Boeing 787 aircraft in 2013. Among the various cathode materials used in these batteries is lithium iron disulfide, Li_2FeS_2 .

(a). State the electron configuration of sulfide.

1 mark

(b). Determine the oxidation number of iron in Li_2FeS_2 .

1 mark

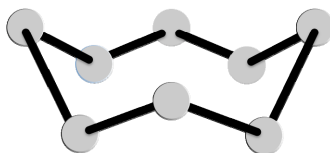
(c). In the rechargeable cell, elemental lithium reacts with lithium iron disulfide to produce elemental iron and lithium sulfide. Write a balanced chemical equation for this reaction.

2 marks

(d). Name the chemical process by which the iron in Li_2FeS_2 is transformed to elemental iron.

1 mark

(e). An essential chemical property of carbon is its ability to *catenate*, *i.e.* to form long chains of carbon atoms bonded to one another. Similarly, sulfur will catenate, though to a lesser extent than carbon. The standard state of sulfur is defined to be S_8 (m.p. 119°C), with the structure shown below.

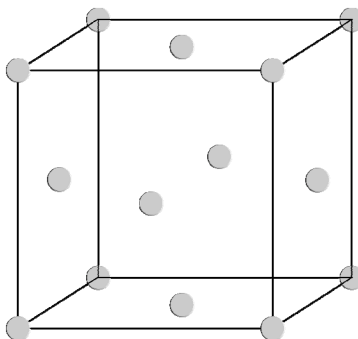


The average bond dissociation enthalpy for a sulfur-sulfur bond in S_8 is $+266\text{ kJ mol}^{-1}$ and the enthalpy of sublimation for S_8 is $+100\text{ kJ mol}^{-1}$. Determine the enthalpy change when one mole of sulfur in its standard state is decomposed into gaseous sulfur atoms.

2 marks

Transition metal disulfides, MS_2 , occur in two broad classes of structure, depending on their bonding. One class consists of two-dimensional metal ion layers sandwiched between sulfide layers. For example, molybdenum – commonly occurring as Mo(IV) – forms MoS_2 , which is used as a lubricant in high temperature and pressure applications. The other class consists of a three-dimensional network structure of metal ions and *discrete disulfide ions*, S_2^{2-} , such as the iron compound, *pyrite*.

For the sake of clarity, iron and sulfur will be referred to as atoms in parts (f) and (g). The crystal structure of *pyrite* reveals a unit cell with a *face-centred cubic* arrangement of iron atoms (see below). In the unit cell, the centre of each iron atom is either located on one of the eight vertices of the cube or in the centre of one of the six faces of the cube (*the sulfur atoms have been omitted for clarity*).



(f). According to the chemical formula of *pyrite* and the unit cell above, determine the *equivalent* number of iron atoms *within* the unit cell and the corresponding number of sulfur atoms that must be located *within* the unit cell.

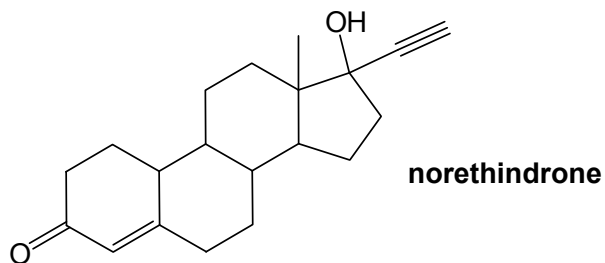
2 marks

(g). Within the unit cell, each iron atom has local octahedral geometry of surrounding sulfur atoms. Each sulfur has local tetrahedral geometry, surrounded by one sulfur atom and the remainder being iron atoms. Sketch each of these geometries below, clearly differentiating between sulfur and iron and indicating relevant bond angles.

3 marks

ORGANIC CHEMISTRY

3. Norethindrone (structure below) is the steroidal hormone that formed the basis of the first oral contraceptive pill. In 1951, it was practically synthesized for the first time in Mexico by Carl Djerassi and coworkers (Djerassi passed away on January 30th 2015 at the age of 91).



(a). How many chirality centres (stereocentres) are present in norethindrone? What is the absolute configuration of the carbon-carbon double bond? (use the descriptor *R*, *Z*, *S* or *E*).

Chirality centres:

Configuration of alkene:

1 mark

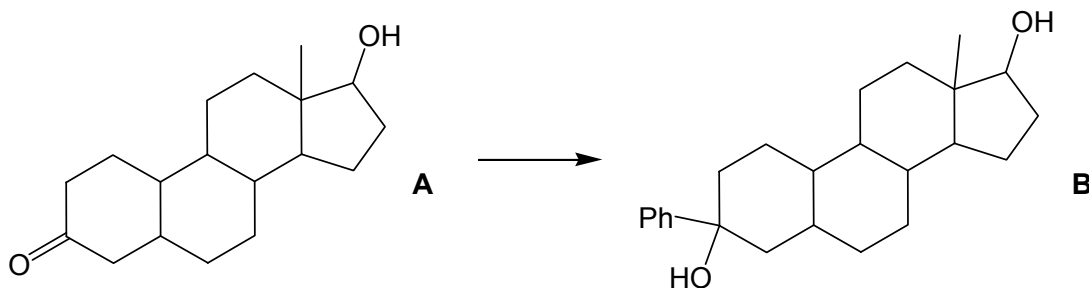
(b). What is the numerical degree of unsaturation present in norethindrone?

1 mark

(c). State the names of the different functional groups found in norethindrone.

2 marks

(d). A similar substance (compound **B**, structure below) was of interest to researchers as an alternative to norethindrone. Compound **B** is to be synthesized from compound **A** via three reaction steps ((i), (ii) and (iii)). Two intermediate compounds (**X** and **Y**) are formed along the pathway from **A** to **B** (note that “Ph” represents a benzene ring in compound **B**).



Draw structures of **X** and **Y** and state reagents needed to accomplish each of the three reaction steps. Draw the structure of the compound formed (**Z**) when **A** is separately reacted with pyridinium chlorochromate.

(i) \longrightarrow	(ii) \longrightarrow	(iii) \longrightarrow
X:	Y:	Z:

6 marks

(d). When compound **B** was synthesized in a research laboratory, a chemist left a sample of it heating overnight in concentrated phosphoric acid. When he returned the next morning, a new substance had formed (**C**). Draw a possible structure for compound **C** below.

2 marks

ANALYTICAL CHEMISTRY

4. A salt is to be analysed for its bromide content. In one trial, a sample of 1.0273 g of the finely ground salt is dissolved in water and treated with excess silver nitrate. Once reaction is complete, the resulting silver bromide precipitate is separated by filtration, washed with cold water, then dissolved in a solution of 0.3 g of $\text{K}_2[\text{Ni}(\text{CN})_4]$ in 1:1 ammonia/ammonium chloride buffer. After diluting to ~150 mL and adding a suitable indicator, the resulting solution was titrated with standard 0.1017 M EDTA, yielding a murexide indicator end-point volume of 14.76 mL.

(a). Write a balanced equation for the *net* reaction between solid silver bromide and the $[\text{Ni}(\text{CN})_4]^{2-}$ anion, given that one of the products is $[\text{Ag}(\text{CN})_2]^-$. What type of reaction is this?

2 marks

(b). What is the relationship between the number of moles of bromide precipitated by the silver nitrate and the number of moles of EDTA used to reach the end-point in the titration, given that metal cations form a 1:1 complex with EDTA?

1 mark

(c). Use this information to calculate the number of moles of bromide present in the mass of sample analysed in this experiment. Show your calculation for full marks.

3 marks

(d). Express the amount of bromide in the sample as a percentage by mass (%w/w).

2 marks

(e). Because the nickel–EDTA complex forms slowly, great care must be taken towards the end of this titration in order to obtain an accurate and reproducible end-point. Zinc forms a more stable complex with EDTA at a much faster rate than nickel, however the $[\text{Zn}(\text{CN})_4]^{2-}$ complex is *more* stable than the $[\text{Ag}(\text{CN})_2]^-$ complex. Suggest a scheme by which the zinc–EDTA reaction *could* be exploited to provide a better end-point than the nickel–EDTA one.

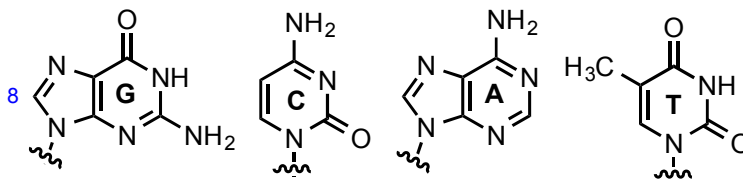
2 marks

(f). It has been noted that reducing species in the sample interfere in this titration. How might this occur, and how would this affect the final result?

2 marks

BIOLOGICAL CHEMISTRY

5. This question is about the enzymes that polymerize deoxyribonucleic acid. DNA is the basis of heritable information transfer for living things. Information is transmitted through a code of just four letters that represent four bases: G, C, A, and T. These letters are then combined with dizzying proportions to build the genomes of different organisms. Below are the chemical structures of the four bases.



(a). Consider that a single DNA polymerase enzyme is able to replicate a strand of B-form DNA (3.4 nm per turn and about 10 base pairs per turn) at 800 nucleotides per second. How long in minutes will it take for the polymerase to copy a specific chromosome (48,129,895 base pairs)? How fast is it moving (in $\mu\text{m/s}$)?

2 marks

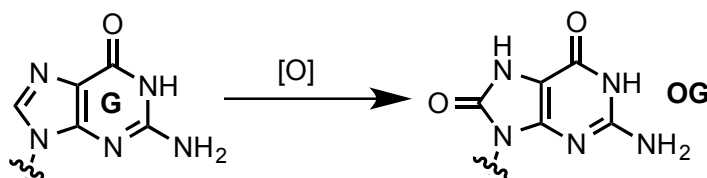
(b). In order to mitigate the impact of mistakes in replication, polymerases in higher organisms have evolved proofreading mechanisms. The error rate for Taq, a commonly-used polymerase that lacks proofreading capabilities, is about 3.0×10^{-4} per base. Consider the case where Taq is responsible for copying your genome once. Assuming that all mutations are uniformly distributed, that there are 19,000 human genes and that only about 2% of genomic DNA encodes those proteins, how many mutations would each gene receive?

1 mark

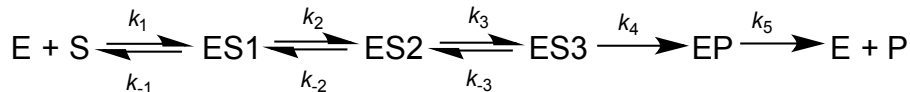
(c). When people think about specificity for a DNA sequence they consider the Watson-Crick base pairing as a mode of base-base recognition. Base-pairing between G and C involves three hydrogen bonds. Draw a GC base pair in the space below, explicitly showing the hydrogen bonds between the two bases.

3 marks

(d). Like other molecules, DNA is prone to chemical degradation. Unfortunately for us, since DNA is the carrier of our heritable information, our cells must find a way to repair damage that might otherwise cause information to be lost. One type of damage is the oxidation of guanosine (G) to 8-oxoguanosine (OG) to form a lesion (abnormality).



In humans, an enzyme called hOGG1 is responsible for the recognition and removal of an OG lesion. hOGG1 removes the damaged base and leaves an “abasic” site. It follows a somewhat complex kinetic expression (below), for which the rate constants have each individually been resolved (see table).



Rate constant (unit)	Mean value
k_1 (?)	2.6×10^8
k_{-1} (s^{-1})	130
k_2 (s^{-1})	13.3
k_{-2} (s^{-1})	1.16
k_3 (s^{-1})	0.012
k_{-3} (s^{-1})	0.07
k_4 (s^{-1})	0.06
k_5 (s^{-1})	0.0064

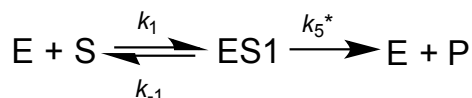
(e). What are the units of k_1 ?

1 mark

(f). What is the rate-limiting step for the removal of an OG lesion by hOGG1 (state both the rate constant and the physical event this corresponds to)?

2 marks

(g). A molecule, P2, was recently discovered as an inhibitor of hOGG1. If we simplify the kinetic scheme to that shown below, we can try to understand the mechanism by which P2 functions.



(h). Provide an expression for the reaction velocity (V) (i.e. the rate) in terms of $[ES1]$. In addition, write the mass-balance equation for the total enzyme concentration, $[E]_{total}$.

2 marks

(i). If the inhibitor P2 is a competitive inhibitor (whose binding is mutually exclusive with the substrate S), would you expect to see a change in the maximal velocity (V_{max}) for hOGG1 upon addition of the inhibitor? Briefly explain.

1 mark

--END OF PART C--



1 H 1.008																	2 He 4.003					
3 Li 6.941	4 Be 9.012	<i>Relative Atomic Masses (2012, IUPAC)</i> <i>*For the radioactive elements the atomic mass of an important isotope is given</i>										<i>Masses Atomiques Relatives (UICPA, 2012)</i> <i>*Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important</i>					5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95					
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80					
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3					
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)					
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (292)	117 Uus	118 Uuo (294)					

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231.0)	92 U (238.0)	93 Np (237)	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 (262)

Symbol **Value**
Symbole *Quantité numérique*

Atomic mass unit	<i>amu</i>	1.66054 x 10 ⁻²⁷ kg	<i>Unité de masse atomique</i>
Avogadro's number	<i>N</i>	6.02214 x 10 ²³ mol ⁻¹	<i>Nombre d'Avogadro</i>
Charge of an electron	<i>e</i>	1.60218 x 10 ⁻¹⁹ C	<i>Charge d'un électron</i>
Dissociation constant (H ₂ O)	<i>K_w</i>	1.00 x 10 ⁻¹⁴ (25°C)	<i>Constante de dissociation de l'eau (H₂O)</i>
Faraday's constant	<i>F</i>	96 485 C mol ⁻¹	<i>Constante de Faraday</i>
Gas constant	<i>R</i>	8.31451 J K ⁻¹ mol ⁻¹ 0.08206 L atm K ⁻¹ mol ⁻¹	<i>Constante des gaz</i>
Mass of an electron	<i>m_e</i>	9.10939 x 10 ⁻³¹ kg	<i>Masse d'un électron</i>
Mass of a neutron	<i>m_n</i>	1.67493 x 10 ⁻²⁷ kg	<i>Masse d'un neutron</i>
Mass of a proton	<i>m_p</i>	1.67262 x 10 ⁻²⁷ kg	<i>Masse d'un proton</i>
Planck's constant	<i>h</i>	6.62608 x 10 ⁻³⁴ J s	<i>Constante de Planck</i>
Speed of light	<i>c</i>	2.997925 x 10 ⁸ m s ⁻¹	<i>Vitesse de la lumière</i>
Rydberg constant	<i>R_∞</i>	1.097 x 10 ⁷ m ⁻¹	<i>Constante de Rydberg</i>

1 Å	= 1 x 10 ⁻¹⁰ m
1 atm	= 101.325 kPa
1 bar	= 1 x 10 ⁵ Pa

STP/TPN	SATP/TPAN
273.15 K	298 K
100 kPa	100 kPa