CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

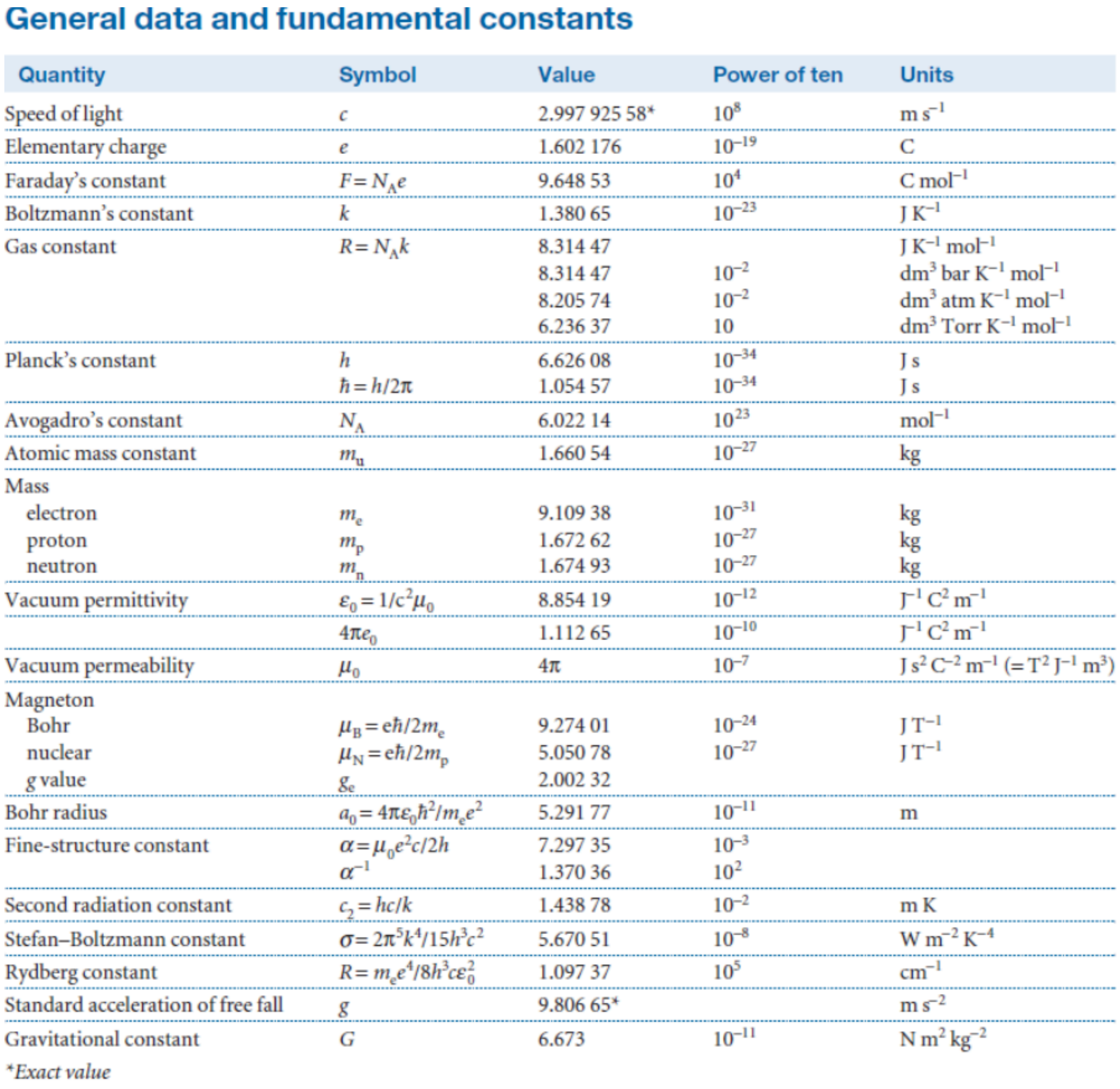
CHEM 342: ATOMIC SPECTROSCOPY

STREAMS: BSC CHEMISTRY **TIME: 2 HOURS**

DAY/DATE: MONDAY 23/12/2024 **8. 30 A.M – 10.30 A.M.**

INSTRUCTIONS:

- ***ANSWER QUESTION ONE AND ANY OTHER TWO QUESTIONS.***



General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	$\mathrm{m\,s^{-1}}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F=N_Ae$	9.648 53	10^{4}	$\mathrm{C\,mol^{-1}}$
Boltzmann's constant	k	1.380 65	10^{-23}	$\mathrm{J\,K^{-1}}$
Gas constant	$R=N_Ak$	8.314 47		$\mathrm{J\,K^{-1}\,mol^{-1}}$
		8.314 47	10^{-2}	$\mathrm{dm^3\,bar\,K^{-1}\,mol^{-1}}$
		8.205 74	10^{-2}	$\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}$
		6.236 37	10	$\mathrm{dm^3\,Torr\,K^{-1}\,mol^{-1}}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar=h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	$\mathrm{mol^{-1}}$
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0=1/c^2\mu_0$	8.854 19	10^{-12}	$\mathrm{J^{-1}\,C^2\,m^{-1}}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$\mathrm{J^{-1}\,C^2\,m^{-1}}$
Vacuum permeability	μ_0	4π	10^{-7}	$\mathrm{J\,s^2\,C^{-2}\,m^{-1}\ (=T^2\,J^{-1}\,m^3)}$
Magneton				
Bohr	$\mu_B=e\hbar/2m_e$	9.274 01	10^{-24}	$\mathrm{J\,T^{-1}}$
nuclear	$\mu_N=e\hbar/2m_p$	5.050 78	10^{-27}	$\mathrm{J\,T^{-1}}$
g value	g_e	2.002 32		
Bohr radius	$a_0=4\pi\varepsilon_0\hbar^2/m_ee^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha=\mu_0e^2c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2=hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma=2\pi^5k^4/15h^3c^2$	5.670 51	10^{-8}	$\mathrm{W\,m^{-2}\,K^{-4}}$
Rydberg constant	$R=m_ee^4/8h^3c\varepsilon_0^2$	1.097 37	10^{5}	$\mathrm{cm^{-1}}$
Standard acceleration of free fall	g	9.806 65*		$\mathrm{m\,s^{-2}}$
Gravitational constant	G	6.673	10^{-11}	$\mathrm{N\,m^2\,kg^{-2}}$

**Exact value*

QUESTION ONE (3O MARKS)

a. (i) Explain why the wave model for radiation cannot account for the photo electric effect

(1 mark)

(ii) Calculate the reflection loss when a beam of radiant energy passes through an empty quartz Cell assuming the refractive index of quartz is 1.55. (1 marks)

(iii) The silver iodide bond energy is approximately 255 Kj/ mol (AgI) is one of the Possible active components in photogray sunglasses). Determine the longest wavelength of light that is capable of breaking the bond in silver iodide. (1.5 marks)

(iv) Cesium is used extensively in photocells and in television cameras because it has the Lowest ionization energy of all the stable elements.

(I) Calculate the maximum kinetic energy of a photoelectron ejected from cesium by 555 Nm light (Note that if the wavelength of the light used to irradiate the cesium surface becomes longer than 660 nm no photoelectrons are emitted) (1.5 marks)

(II) Use the rest mass of the electron to calculate the velocity of the photoelectron in (I) (1 mark)

b. (i) Contrast spontaneous and stimulated emission (2 marks)

(ii) A monochromator with a focal length of 0.78 m was equipped with an echellete grating Of 2500 blazes per millimeter.

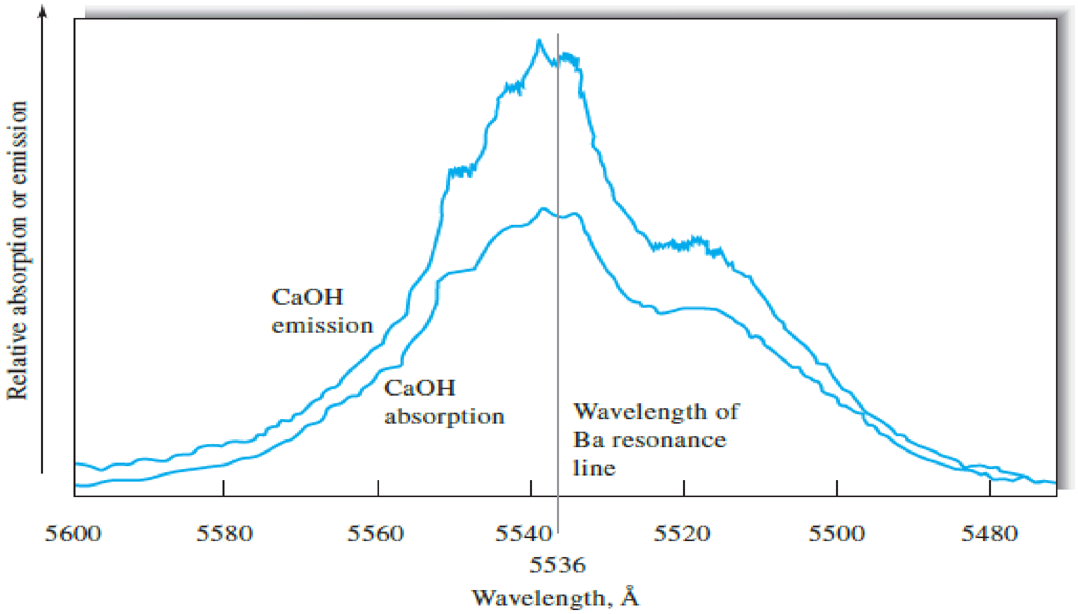
(I) Calculate the reciprocal linear dispersion of the instrument for first order spectra. (0.5 mark)

(II) Determine the first order resolving power of the monochromator given 2 cm of the grating were illuminated (0.5 mark)

(III) Calculate the minimum wavelength difference that could in theory be completely resolved by the instrument at approximately 430 nm (0.5 mark)

(iii) Describe the basis for radiation detection with a silicon diode transducer (1 mark)

c. (i) Explain as to why the caolt spectrum in figure below is so much broader than the barium emission line (1 mark)



(ii) Explain the following observations

(I) In a hot flame, the emission intensities of the sodium lines at 589.0 and 589.6 nm are greater in a sample solution that contains KCl than when this compound is absent

(1 mark)

(II) The intensity of a line for atomic Cs is much lower in a natural gas flame, which operates at 1800^{0}C, than in a hydrogen- oxygen flame, whose temperature is 2700^{0}C. (1 mark)

(III) In the concentration range of 500 to 2000 ppm of U, there is a linear relationship between absorbance at351.5 nm and concentration. At lower concentrations the relationship is nonlinear unless about 2000 ppm of an alkali metal salt is introduced into the sample. Explain. (1 mark)

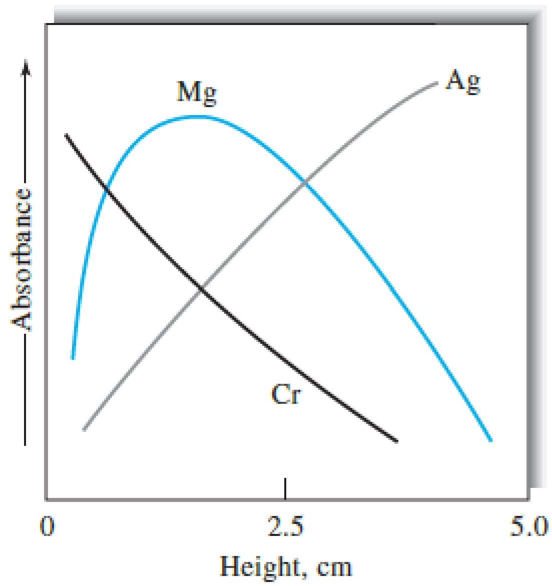
(iii) Distinguish the following:

(I) Spectral interference and chemical interference (1 mark)

(II) Sputtering and Doppler broadening (1 mark)

d. (i) Describe the effects that are responsible for the three different absorbance profiles in the figure below and select three additional dements you would expect to have similar profiles

(2 marks)



(ii) With the help of a suitable diagram describe how a deuterium lamp can be used to provide backgroundcorrection for an atomic absorption spectrum. (2 marks)

(iii) State the reason as to why source modulation used in atomic absorption spectroscopy

(0.5 mark)

(iv) Describe why atomic emission is more sensitive to flame instability than atomic absorption or fluorescence (3 marks)

(v) Explain the reason as to why a continuous source like D_2 lamp or tungsten lamp cannot be used in atomic absorption spectroscopy. (2.5 marks)

e. (i) Briefly explain the reason as to why the internal-standard method is often used in plasma emission spectrometry. (1 mark)

(ii) It is observed that in a hot flame the emission intensities of the sodium lines at 589 and 589.6 are greater in a sample solution that contains KCl than when this compound is Absent. Suggest an explanation. (1.5 marks)

(iii) Outline the types of interferences that are encountered in atomic mass spectrometry

(1 mark)

QUESTION TWO (20 MARKS)

a. (i) The mass absorption coefficient for Ni, measured with the Cu Kα line, is 49.2 cm^2/g. Calculate the thickness of a nickel foil that was found to transmit 47.8% of the incident Power of a beam of Cu Kα radiation. The density of Ni is 8.90 g/cm^3 (1 mark)

(ii) For Na atoms and Mg+ ions, compare the ratios of the number of particles in the 3p excited state to the number in the ground state in (4 marks)

(I) A natural gas-air flame (2100K)

(II) A hydrogen-oxygen flame (2900K)

(III) An inductively coupled plasma source (6000k)

(iii) The Doppler effect is one of the sources of the line broadening in atomic absorption Spectroscopy. Atoms moving toward the light source encounter higher-frequency radiation than atoms moving away from the source. The difference in wavelength Δλ experienced by an atom moving at speed *v* (compared to one at rest) is $\Delta\lambda/\lambda = v/c$, where *c* is the velocity of light. Estimate the line width (in nanometers) of the lithium line at 670.776 (6707.76 Å) when the absorbing atoms are at a temperature of (a) 2000 K and (b) 3120 K. The average speed of an atom is given by $v = \sqrt{\frac{8kT}{\Pi m}}$, where *k* is Boltzmann's constant, *T* is the absolute temperature, and *m* is its mass.

(2 marks)

(iv) A 5.00 ml sample of blood was treated with trichloroacetic acid to precipitate proteins after centrifugation, the resulting solution was brought to a pH of 3 and was extracted with two 5- mL portions of methyl isobutyl ketone containing the organic lead Complexing agent APCD. The extract was aspirated directly into an air-acetylene flame yielding an absorbance of 0.444 at 283.3 nm. Five milliliter aliquots of standards solutions containing 0.250 and 0.450 ppm Pb were treated in the same way and yielded absorbances of 0.396 and 0.599. Calculate the concentration Pb (ppm) in the sample assuming that Beer's law is followed. (3 marks)

b. (i) State seven advantages as to why carbon is used as an electrode in arc and spark sources

(3.5 marks)

(ii) Outline the relative advantages and disadvantages of ICP torches and dc argon torches

(4 marks)

(iii) Describe the interface between the ICP torch and the mass spectrometer in an ICPMS Instrument (2.5 marks)

QUESTION THREE (20 MARKS)

a. Among the numerous commercial derivatives of ethylenediaminetetracetic acid (EDTA), a mixed salt of Zn/Na containing one atom of zinc and two atoms of sodium per molecule of EDTA is found. This mixed salt presents itself in the form of a crystallized hydrate. An attempt is described to deduce the number of water molecules of this hydrate by measuring the presence of zinc by atomic absorption. The experimental approach was as follows: A solution A, is prepared by dissolving 35.7 mg of the hydrate in 100 mL of water. 2 mL were then pipetted and diluted again with H2O to a final volume of 100 mL. This constitutes the sample solution The standardization is then performed with five solutions of known Zinc concentration

i. Describe what this parameter represent in effecting the measurement the slit bandwidth of the atomic absorption apparatus is 1 nm. (1 mark)

ii. Knowing that the calibration curve computed by the apparatus indicates that A = 0.3692, C = 0.99mg/L, calculate the number of molecules of water in the mixed salt hydrate of Zn/Na. (1 mark)

iii. From the data and by the method of least squares derive an equation for the calibration curve. Calculate the zinc concentration in solution A. Recall: H = 1.01; N = 14.01; O = 16.0; Na = 22. 99 and Zn = 65.39 g/mol respectively. (3 marks)

iv. State whether the use of the standard calibration curve justified for atomic absorption. (1 mark)

Solution	Conc. Zn mg/L	Absorbance
Blank	0.00	0.0006
Standard 1	0.50	0.2094
Standard 2	0.75	0.2961
Standard 3	1	0.3674
Standard 4	1.25	0.4333
Standard 5	1.5	0.4817
Standard 6	C	0.3692

b. (i) Describe the working principle of a time of flight mass spectrometer (4 marks)

(ii) A $^{35}Cl^{+}$ ion travels through the flight tube of TOF mass spectrometer with a kinetic energy of 3.65×10^{-16} J. This ion takes 1.04×10^{-5} S to reach the detector. Avogadro's constant (L) = 6.022 × 10^{23} mol-1 calculate the length of the flight tube in meters (1.5 marks)

(iii) Explain why it is easier to measure traces of radioactive, α-emitting isotopes of long half-life by ICP/MS rather than by radioactivity counting. (2.5 marks)

(iv) Write short notes on Zeeman effects in atomic spectroscopy include also advantages and disadvantages of the method. (4 marks)

(v) Explain why a matrix modifier is added when using graphite furnace atomic absorption Spectroscopy during analysis. (2 marks)

QUESTION FOUR (20 MARKS)

a. (i) Write short notes on the mole ratio method for the determination of the composition of a complex (1 mark)

(ii) The sodium salt of 2-quinizarinsulfonic acid (NaQ) forms a complex with Al^{3+} that absorbs radiation strongly at 560 nm. Use the data from Owens and Yoe's paper given below to answer the following questions

c_Q,M	A_{560}
1.00×10^{-5}	0.131
2.00×10^{-5}	0.265
3.00×10^{-5}	0.396
4.00×10^{-5}	0.468
5.00×10^{-5}	0.4876
6.00×10^{-5}	0.498
8.00×10^{-5}	0.499
1.00×10^{-4}	0.500

I. Find the formula of the complex. In all solutions, C_{Al}= 3.7 × 10^{-5}, and all measurements were made in 1.00-cm cells. (1 mark)

II. Calculate an average value for the molar absorptivity of the complex assume that in the linear portion of the plot the metal is completely completed. (1 mark)

III. Determine the degree of dissociation. (2 marks)

IV. Calculate a value of Kj for the complex based upon the stoichiometric relationship that exist under conditions of maximum absorption. (1 mark)

V. Calculate Gibbs free energy of the formation of the complex. (1 mark)

(ii) Chromium (Cr) in an aqueous sample was determined by pipetting 10.0 mL of the unknown

into each of five 50.0 mL volumetric flasks. The volumes (indicated below) of standard

containing 12.2 ppm Cr were added into the flasks and each solution was made up to volume.

The plot gave a linear equation of y = 0.0088x + 0.2022

Unknown volume(mL)	Standard volume (mL)	Absorbance
10.0	0.0	0.201
10.0	10.0	0.292
10.0	20.0	0.378
10.0	30.0	0.467
10.040.0		0.554

I. Determine an equation for relationship between absorbance and volume of standard

(1 marks)

II. Calculate the statistics for the least squares relationship in I above

(2 marks)

III. Determine the concentration of Cr in ppm in the sample (1 marks)

b) The acid-base indicator HIn undergoes the following reaction in dilute aqueous solution:

$HIn \leftrightharpoons H^{+} + In^{-}$

color 1 color 2

The following absorbance data were obtained for a 5.0×10^{-4} M solution of HIn in 0.1 M NaOH and0.1 M HCl. Measurements were made at wavelengths of 485 nm and 625 nm with 1.00 cm cells.

0.1 M NaOHA_{485}=0.075A_{625} = 0.904
0.1 M HCl A_{485} =0.487 A_{625} =0.181

In the NaOH solution, essentially all of the indicator is present as In^{-}; in the acidic solution, it Is essentially all in the form of HIn.

i. Calculate molar absorptivities for In^{-} and HIn at 485 and 625 nm. (1 marks)
ii. Calculate the acid dissociation constant for the indicator if a pH 5.00 buffer containing a small amountof the indicator exhibits an absorbance of 0.567 at 485 nm and 0.395 at 625 nm (1.00-cm cells). (2 marks)

iii. What is the pH of a solution containing a small amount of the indicator that exhibits an absorbance of 0.492 at 485 nm and 0.245 at 635 nm (1.00-cm cells) (2 marks)

iv. A 25.00-mL aliquot of a solution of purified weak organic acid HX required exactly 24.20 mL of a standard solution of a strong base to reach a phenolphthalein end point. When exactly 12.10 mL of the base was added to a second 25.00-mL aliquot of the acid, which contained a small amount of the indicator under consideration, the absorbance was found to be 0.333 at 485 nm and 0.655 at 625 nm (1.00-cm cells). Calculate the pH of the solution and K_a for the weak acid. (2 marks)

v. What would be the absorbance of a solution at 485 and 625 nm (1.50-cm cells) that was 2.00×10^{-4} M in the indicator and was buffered to a pH of 6.000? (1 marks)

(c) The following data were obtained for a voltage measurement in mv, on a noisy system: 1.37, 1.84, 1.35, 1.47, 1.10, 1.73, 1.54, 1.08 (1 marks)

(i) Assuming the noise is random, determine the signal to noise ratio

(ii) Calculate the number of measurements would have to be averaged to increase S/N to 10

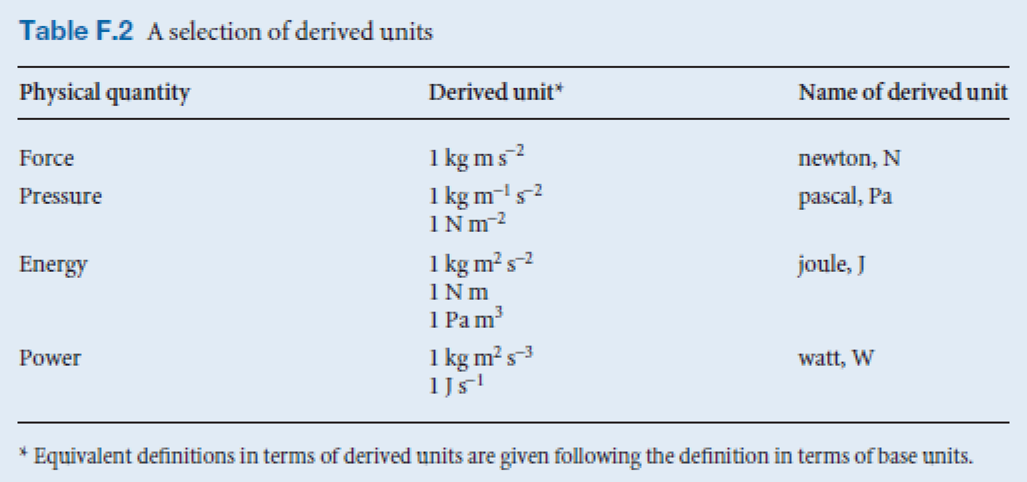


Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	1 kg m^{-1} s^{-2} 1 N m^{-2}	pascal, Pa
Energy	1 kg m^2 s^{-2} 1 N m 1 Pa m^3	joule, J
Power	1 kg m^2 s^{-3} 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

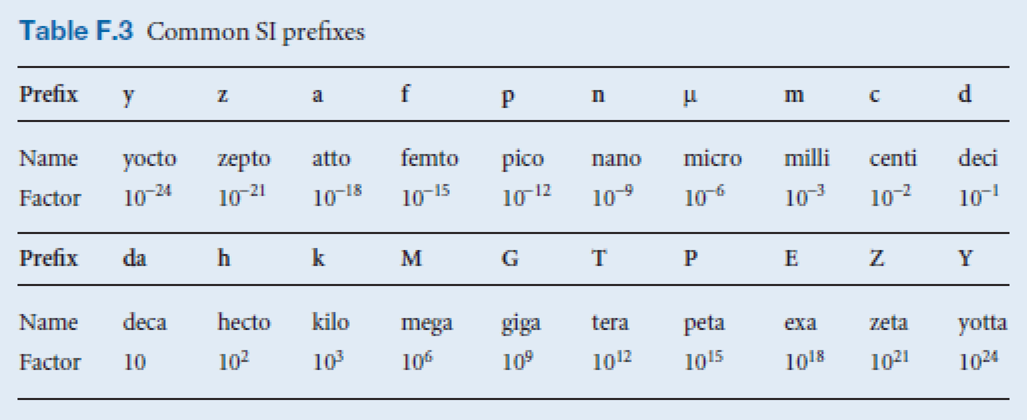
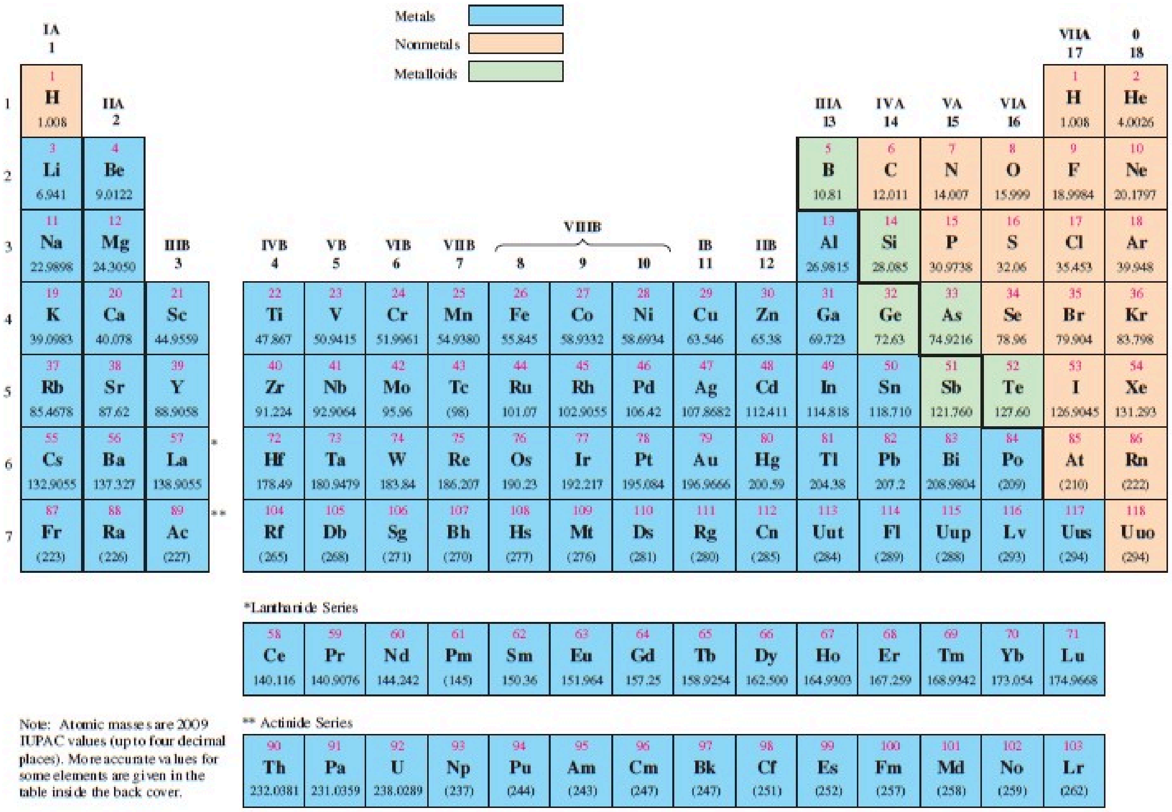


Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	µ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}
Prefix	**da**	**h**	**k**	**M**	**G**	**T**	**P**	**E**	**Z**	**Y**
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^{2}	10^{3}	10^{6}	10^{9}	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

PERIODIC TABLE OF THE ELEMENTS



Metals 🟦

Nonmetals 🟧

Metalloids 🟩

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.008																1 **H** 1.008	2 **He** 4.0026
2	3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.9984	10 **Ne** 20.1797
3	11 **Na** 22.9898	12 **Mg** 24.3050											13 **Al** 26.9815	14 **Si** 28.085	15 **P** 30.9738	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.845	27 **Co** 58.9332	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9058	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.96	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.293
6	55 **Cs** 132.9055	56 **Ba** 137.327	57 **La** 138.9055 *	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.9666	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227) **	104 **Rf** (265)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Uut** (284)	114 **Fl** (289)	115 **Uup** (288)	116 **Lv** (293)	117 **Uus** (294)	118 **Uuo** (294)

*Lanthanide Series

58 **Ce** 140.116	59 **Pr** 140.9076	60 **Nd** 144.242	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.500	67 **Ho** 164.9303	68 **Er** 167.259	69 **Tm** 168.9342	70 **Yb** 173.054	71 **Lu** 174.9668

** Actinide Series

90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	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)

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.