NATIONAL UNIVERSITY OF LESOTHO

FACULTY OF SCIENCE AND TECHNOLOGY

Department of Chemistry and Chemical Technology

BSc, BSc Chem. Tech. And BSc Ed Final Examination

C3740– Physical Chemistry II

June 15, 2023

Duration: 3 hours

This Exam contains 5 pages (including this cover page) and 5 questions. Total of points is 80. Page 2 contains the table of physical constants and the periodic table is on page 3. Good luck!

Distribution of Marks

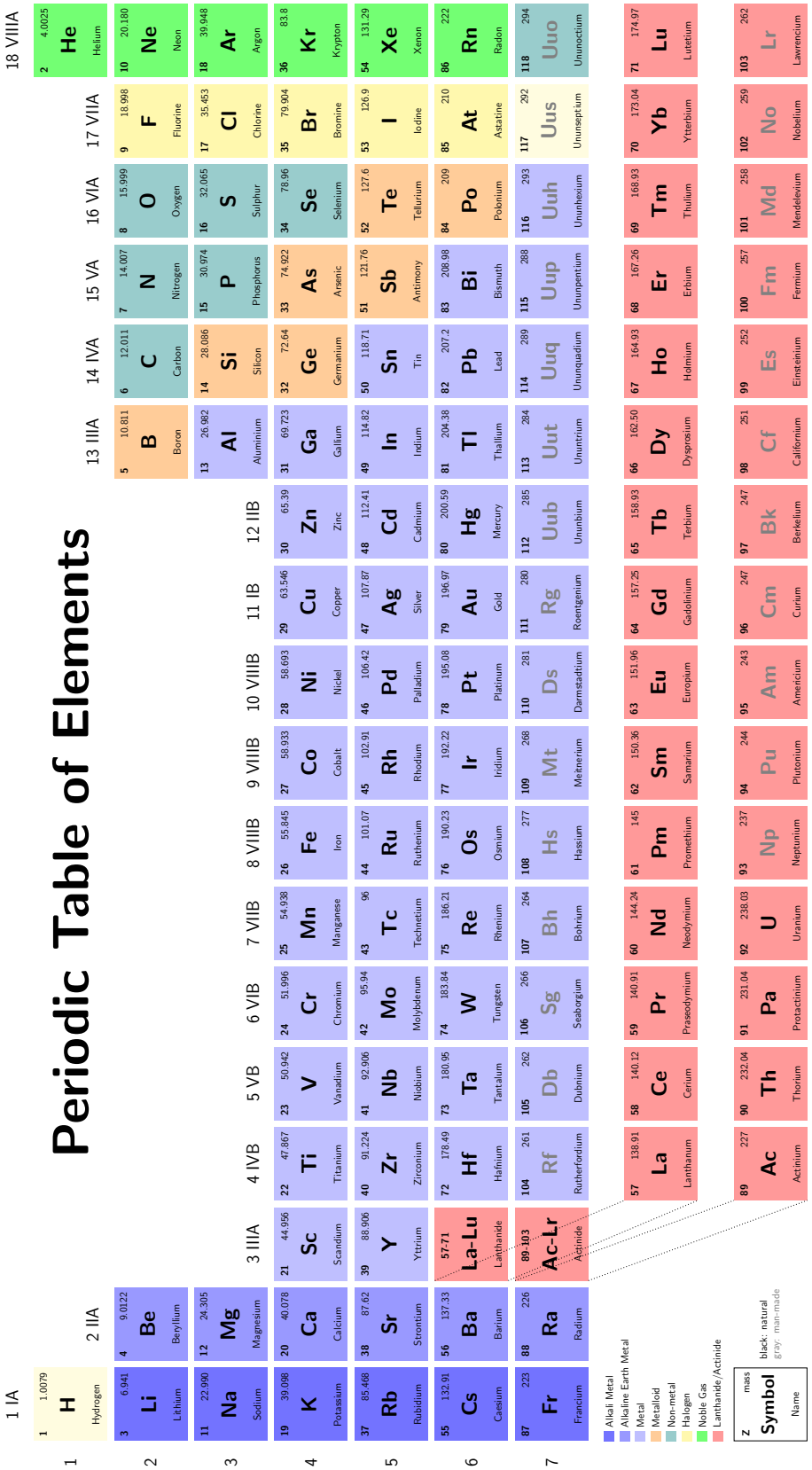
Question:	1	2	3	4	5	Total
Points:	20	20	20	15	5	80

Quantity	*Symbol*	*Value*[a,b]	*Units*
Acceleration due to gravity	g	9.806 65 (exact)	$m\ s^{-2}$
Speed of light in vacuum	c	299 792 458 (exact)	$m\ s^{-1}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ (exact)	$N\ A^{-2}$
		$= 12.566\ 370\ 614\ldots$	$10^{-7}\ N\ A^{-2}$
Permittivity of vacuum	ϵ_0	$1/\mu_0 c^2$ (exact)	$C^2\ N^{-1}\ m^{-2}$
		$= 8.854\ 187\ 817\ldots$	$10^{-12}\ C^2\ N^{-1}\ m^{-2}$
Planck constant	h	6.626 075 5(40)	$10^{-34}\ J\ s$
$h/2\pi$	$\hbar$	1.054 572 66(63)	$10^{-34}\ J\ s$
Elementary charge	e	1.602 177 33(49)	$10^{-19}\ C$
Bohr magneton, $e\hbar/2m_e$	μ_B	9.274 015 4(31)	$10^{-24}\ J\ T^{-1}$
Nuclear magneton, $e\hbar/2m_p$	μ_N	5.050 786 6(17)	$10^{-27}\ J\ T^{-1}$
Rydberg constant, $m_e e^4/8h^3 c\epsilon_0$	R_∞	10 973 731.534(13)	m^{-1}
Bohr radius, $h^2\epsilon_0/\pi m_e e^2$	a_0	0.529 177 249(24)	$10^{-10}\ m$
Hartree energy, $e^2/4\pi\epsilon_0 a_0$	E_h	4.359 748 2(26)	$10^{-18}\ J$
Electron mass	m_e	9.109 389 7(54)	$10^{-31}\ kg$
Proton mass	m_p	1.672 623 1(10)	$10^{-27}\ kg$
Neutron mass	m_n	1.674 928 6(10)	$10^{-27}\ kg$
Deuteron mass	m_d	3.343 586 0(20)	$10^{-27}\ kg$
Avogadro constant	N_A	6.022 136 7(36)	$10^{23}\ mol^{-1}$
Atomic mass constant, $m_u = (1/12)m(^{12}C)$	m_u	1.660 540 2(10)	$10^{-27}\ kg$
Faraday constant	F	96 485.309(29)	$C\ mol^{-1}$
Gas constant	R	8.314 510(70)	$J\ K^{-1}\ mol^{-1}$
		0.083 145 1	$L\ bar\ K^{-1}\ mol^{-1}$
		1.987 216	$cal\ K^{-1}\ mol^{-1}$
		0.082 057 8	$L\ atm\ K^{-1}\ mol^{-1}$
Boltzmann constant, R/N_A	k	1.380 658(12)	$10^{-23}\ J\ K^{-1}$

[a] E. R. Cohen and B. N. Taylor, The 1986 CODATA Recommended Values of the Fundamental Physical Constants. *J. Phys. Chem. Ref. Data* **17**:1795 (1988).

[b] Digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.

[c] More recent values of physical constants are available on the Web site of the National Institute of Standards and Technology (http://physics.nist.gov/constants).


Periodic Table of Elements
1 IA
2 IIA
3 IIIA
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H Hydrogen
2 4.0025 He Helium
3 6.941 Li Lithium
4 9.0122 Be Beryllium
5 10.811 B Boron
6 12.011 C Carbon
7 14.007 N Nitrogen
8 15.999 O Oxygen
9 18.998 F Fluorine
10 20.180 Ne Neon
11 22.990 Na Sodium
12 24.305 Mg Magnesium
13 26.982 Al Aluminium
14 28.086 Si Silicon
15 30.974 P Phosphorus
16 32.065 S Sulphur
17 35.453 Cl Chlorine
18 39.948 Ar Argon
19 39.098 K Potassium
20 40.078 Ca Calcium
21 44.956 Sc Scandium
22 47.867 Ti Titanium
23 50.942 V Vanadium
24 51.996 Cr Chromium
25 54.938 Mn Manganese
26 55.845 Fe Iron
27 58.933 Co Cobalt
28 58.693 Ni Nickel
29 63.546 Cu Copper
30 65.39 Zn Zinc
31 69.723 Ga Gallium
32 72.64 Ge Germanium
33 74.922 As Arsenic
34 78.96 Se Selenium
35 79.904 Br Bromine
36 83.8 Kr Krypton
37 85.468 Rb Rubidium
38 87.62 Sr Strontium
39 88.906 Y Yttrium
40 91.224 Zr Zirconium
41 92.906 Nb Niobium
42 95.94 Mo Molybdenum
43 96 Tc Technetium
44 101.07 Ru Ruthenium
45 102.91 Rh Rhodium
46 106.42 Pd Palladium
47 107.87 Ag Silver
48 112.41 Cd Cadmium
49 114.82 In Indium
50 118.71 Sn Tin
51 121.76 Sb Antimony
52 127.6 Te Tellurium
53 126.9 I Iodine
54 131.29 Xe Xenon
55 132.91 Cs Caesium
56 137.33 Ba Barium
57-71 La-Lu Lanthanide
72 178.49 Hf Hafnium
73 180.95 Ta Tantalum
74 183.84 W Tungsten
75 186.21 Re Rhenium
76 190.23 Os Osmium
77 192.22 Ir Iridium
78 195.08 Pt Platinum
79 196.97 Au Gold
80 200.59 Hg Mercury
81 204.38 Tl Thallium
82 207.2 Pb Lead
83 208.98 Bi Bismuth
84 209 Po Polonium
85 210 At Astatine
86 222 Rn Radon
87 223 Fr Francium
88 226 Ra Radium
89-103 Ac-Lr Actinide
104 261 Rf Rutherfordium
105 262 Db Dubnium
106 266 Sg Seaborgium
107 264 Bh Bohrium
108 277 Hs Hassium
109 268 Mt Meitnerium
110 281 Ds Darmstadium
111 280 Rg Roentgenium
112 285 Uub Ununbium
113 284 Uut Ununtrium
114 289 Uuq Ununquadium
115 288 Uup Ununpentium
116 293 Uuh Ununhexium
117 292 Uus Ununseptium
118 294 Uuo Ununoctium
57 138.91 La Lanthanum
58 140.12 Ce Cerium
59 140.91 Pr Praseodymium
60 144.24 Nd Neodymium
61 145 Pm Promethium
62 150.36 Sm Samarium
63 151.96 Eu Europium
64 157.25 Gd Gadolinium
65 158.93 Tb Terbium
66 162.50 Dy Dysprosium
67 164.93 Ho Holmium
68 167.26 Er Erbium
69 168.93 Tm Thulium
70 173.04 Yb Ytterbium
71 174.97 Lu Lutetium
89 227 Ac Actinium
90 232.04 Th Thorium
91 231.04 Pa Protactinium
92 238.03 U Uranium
93 237 Np Neptunium
94 244 Pu Plutonium
95 243 Am Americium
96 247 Cm Curium
97 247 Bk Berkelium
98 251 Cf Californium
99 252 Es Einsteinium
100 257 Fm Fermium
101 258 Md Mendelevium
102 259 No Nobelium
103 262 Lr Lawrencium
Alkali Metal
Alkaline Earth Metal
Metal
Metalloid
Non-metal
Halogen
Noble Gas
Lanthanide/Actinide
Z mass
Symbol
Name
black: natural
gray: man-made

1. (a) Why are $\Delta_{fus}S$ and $\Delta_{vap}S$ always positive? (3)

   (b) Under what conditions does the equality $\Delta S = \Delta H/T$ hold? (3)

   (c) Calculate the change in entropy of 2.00 moles of $H_2O_{(l)}$ ($\bar{C}_p = 75.2\ JK^{-1}mol^{-1}$) if it is heated from 10 °C to 95 °C. (4)

   (d) Assume a bottle contains 25 ml of H_2O (l) at 20 °C. What will be the volume of the H_2O (l) at 50 °C? Take the thermal expansion coefficient, $\alpha = 2.1 \times 10^{-4}\ K^{-1}$. (5)

   (e) Derive the equation

$$\left(\frac{\partial(A/T)}{\partial T}\right)_V = -\frac{U}{T^2}$$

   which is a Gibbs-Helmholtz equation for A. (5)

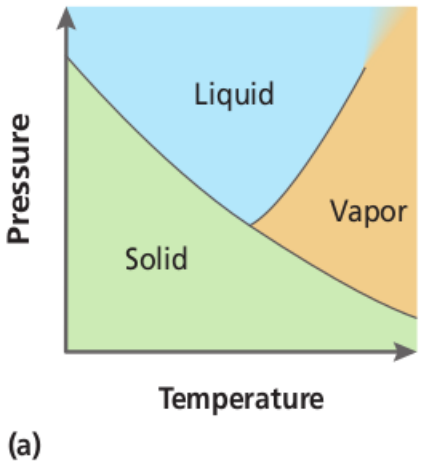
2. (a) State the Clapeyron equation and explain how it is used to determine the slope of a phase boundary on a phase diagram. (5)

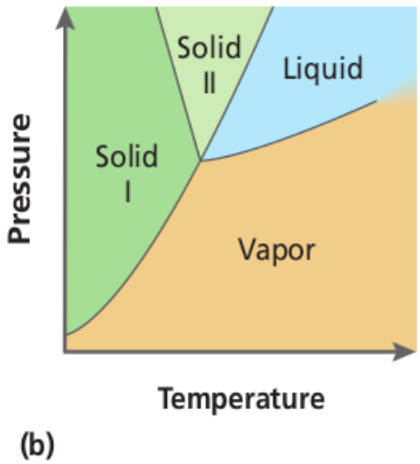
   (b) The vapour pressure of solid ammonia in torr is found to obey the equation

$$ln(P/torr) = -\frac{4124.4\ K}{T} - 1.81630\ln(T/K) + 34.4834$$

   from 146 K to 195 K. Calculate the molar enthalpy of sublimation of ammonia in this temperature range. (5)

   (c) Are the two $P-T$ phase diagrams shown below likely to be observed for a pure substance? Explain your answer. Provide **separate answers** for both diagrams. (10)





3. (a) For an ideal binary solution that obeys Raoult's law, show that

$$P_{Tot} = P_B^* + X_A(P_A^* - P_B^*)$$

Sketch and label a plot of P_{Tot} *vs* X_A for such a solution. (5)

(b) At 325 K, pure toluene and haxane have vapour pressure of 1.42×10^4 Pa and 5.77×10^4 Pa, respectively.
(i) Calculate the mole fraction of hexane in the liquid mixture that boils at a pressure of 0.400 atm.
(ii) Calculate the mole fraction of hexane in the vapour that is in equilibrium with the liquid part of (a). (10)

(c) In an ideal solution of A and B, 2.50 mol are in the liquid phase and 4.75 mol are in the gaseous phase. The overall composition of the system is $Z_A = 0.250$ and $X_A = 0.175$. Calculate Y_A.

Hint: Use the Lever rule for calculating amounts of vapour and liquid in coexistence region $n_{liq}^{tot}(Z_B - X_B) = n_{vap}^{tot}(Y_B - Z_B)$. (5)

4. (a) The gas phase decomposition of dimethyl ether (CH_3OCH_3) to methane (CH_4), hydrogen (H_2), and carbon monoxide (CO) is a first order reaction.

$$CH_3OCH_3\,(g) \rightarrow CH_4\,(g) + H_2\,(g) + CO\,(g)$$

Define the rate of reaction with respect to the pressure of the reactant. (5)

(b) The decomposition of N_2O_5 is an important process in tropospheric chemistry. The half-life for the first-order decomposition of this compound is 2.05×10^4 s. How long will it take for N_2O_5 to decay to 60% of its initial concentration? (5)

(c) For the acid-catalyzed hydrolysis of penicillin, a NUL professor collected kinetic data and plotted ln(k) versus 1/T as a scatter plot. The resulting linear least squares curve has an equation of

$$\ln(k) = (-6300)\frac{1}{T} + 14.1$$

For this reaction, find the
(i) activation energy, Ea, and
(ii) pre-exponential factor, A. (5)

5. A sample of an isotope of francium initially has 128 moles of nuclides (at $t = 0.0s$). Only 8.0 moles of francium remain at $t = 20s$. At what time does the sample have only 2 moles of francium nuclides left?
Choose 1 answer:

A. $t = 30s$
B. $t = 40s$
C. $t = 35s$
D. $t = 25s$

Show your work for the answer chosen. (5)