FACULTY OF CALGARY FACULTY OF SCIENCE MIDTERM EXAMINATION CHEMISTRY 351

Version

1

Time: 2 Hours

Wed Oct 29th, 2025

READ ALL THE INSTRUCTIONS CAREFULLY PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON <u>BOTH</u> YOUR WRITTEN ANSWER SHEET AND COMPUTER ANSWER SHEET. ENTER VERSION NUMBER 1 ON BOTH ANSWER SHEETS

The examination consists of **Parts 1-7**, each of which should be attempted. Note that some parts provide you with a choice of questions, *e.g.* answer 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. **Parts 1-4** will be computer graded, and **Parts 5-7** are to be answered **IN BLUE or BLACK INK or DARK PENCIL** (HB or darker) **IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED**.

Parts 1-4 consist of a series of multiple choice questions numbered 1-31 to be answered on the computer answer sheet (no extra time is provided for "bubbling" in). Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a *pencil only* and *not ink*. In some cases it is required that you indicate *multiple* items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out *both* space A and space B. Part marks may be awarded in some questions. Incorrect answers must be erased *cleanly*.

A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages

Molecular models and calculators are permitted, <u>but NOT programmable calculators</u>. Absolutely no other electronic devices are allowed.

14% PART 1: RELATIVE PROPERTIES

ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most etc. first) with respect to the indicated property.

Use the following code to indicate your answers.

- A. i > ii > iii D. ii > iii > i
 B. i > iii > ii E. iii > i > i
 C. ii > i > iii AB. iii > ii
- 1. The relative strengths of the indicated bonds:

2. The relative importance of the following resonance contributors:

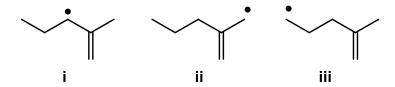
3. The relative basicity of the following compounds:

$$\bigcap$$
 CN \bigcap NH₂ \bigcap \bigcap H₃

4. The relative energies of the following conformations:

Use the following code to indicate your answers.

- **5.** The relative stability of the following radicals:



6. The relative yields of the following chloropentanes formed by the reaction of pentane with chlorine in the presence of uv light:

7. The relative acidity of the most acidic H in each of the following:

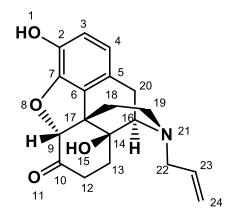
8. The relative concentration of each of the following species present in an aqueous solution at pH = 2.5:

18% PART 2: MOLECULAR PROPERTIES

ANSWER ALL of the questions 9 - 17

For each of the questions 9 - 17 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

Questions 9-17 all refer an opioid antagonist (structure shown below):



- 9. Which atom is the most acidic hydrogen bonded to?
 - **A.** 01
- **B.** C9
- **C**. C12
- **D.** O15
- **E.** C22
- **10**. What type of orbitals do the lone pairs of **O11** and **N21** occupy respectively?

A.
$$sp^3$$
, sp^3 **B.** sp^2 , sp^3 **C.** p , sp^3 **D.** sp^3 , sp^2 **E.** sp^2 , sp^2 **AB**. sp^3 , p

B.
$$sp^2$$
, sp^3

$$\mathbf{C}$$
. p, sp³

$$\mathbf{D}$$
. sp³, sp²

E.
$$sp^2$$
, sp^2

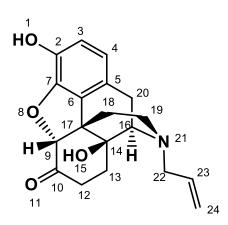
- 11. What are the hybridisations of O1 and C24 respectively?

A.
$$sp^3$$
, sp^3

B.
$$sp^2$$
, sp^3 **C.** sp^3 , sp^2 **D.** sp^2 , sp^2

$$\mathbf{D}$$
. sp^2 , sp^2

- E. sp, sp
- 12. What is the IHD (index of hydrogen deficiency) of this compound?
 - **A.** 7
- **B.** 8
- **C.** 9
- **D.** 10
- **E.** 11



- **13**. Which of the following functional group(s) are found in the compound?
 - A. amine
- B. amide
- C. aldehyde
- D. ester
- E. ether
- 14. What configuration terms best describe C9 and the C23=C24 respectively?
 - **A.** R, E
- **B.** R, Z
- **C.** S, E
- **D.** S, Z
- E. R only
- **AB**. S only

- 15. Which of the bonds listed below is the shortest?
 - **A.** C2-C3
- **B.** C3-C4
- **C**. C6-C17
- **D.** C16-C20
- E. C23-C24
- **16**. If the compound were reacted with an equivalent of HCI, where would it protonate and to approximately what percentage ?
 - **A**. O1 (~50%)
- **B**. O1 (~100%)
- **C**. O15 (~50%)
- **D**. O15 (~100%)

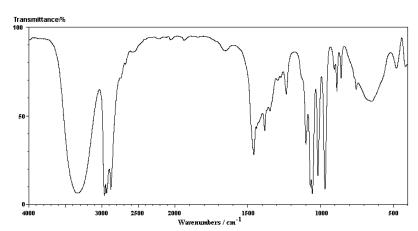
- E. N21 (~50%)
- **AB**. N21 (~100%)
- 17. Which term(s) best describes C22?
 - A. allylic
- **B.** benzylic
- C. primary
- **D.** secondary
- E. tertiary

15% PART 3: SPECTROSCOPY

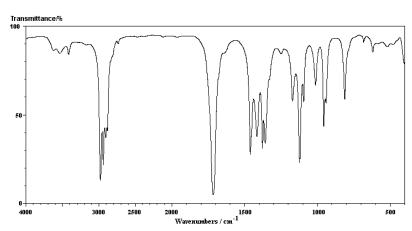
ANSWER ALL SIX (6) OF QUESTIONS 18 - 23 (2.5 marks per question).

For each of the questions 18-23, match the IR spectra to a structure in the list below:

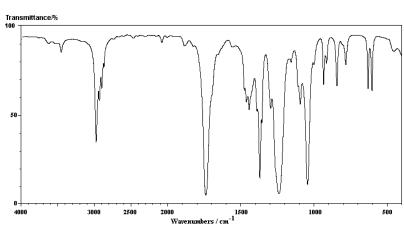
18.



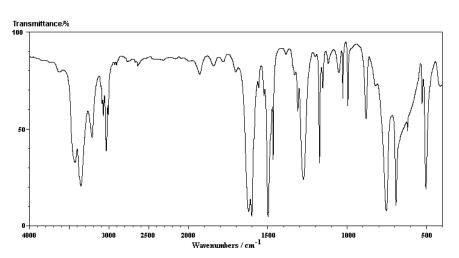
19.



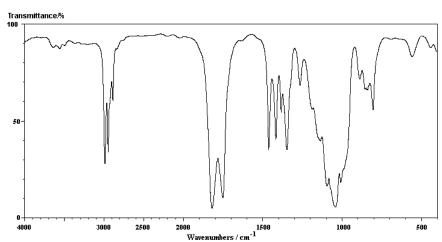
20.



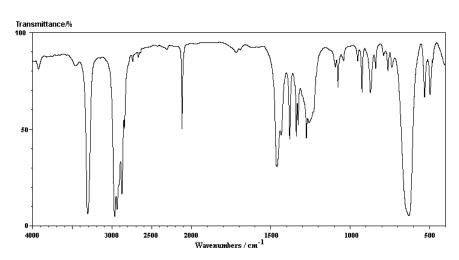
21.



22.



23.



14% PART 4: NOMENCLATURE

ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question). For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.

A. 3-propyl-4-(1,1-dimethylethyl)-heptane

B. 4-ethyl-5-t-butyloctane

C. 4-(1,1-dimethylethyl)-5-ethyloctane

D. 4-(1,1-dimethylethyl)-3-propylheptane

E. 5-(1,1-dimethylethyl)-4-propylheptane

AB. 5-ethyl-4-(1,1-dimethylethyl)-octane

25.

A. (E)-2-ethylpent-3-enenitrile

B. (Z)-2-ethylpent-3-enenitrile

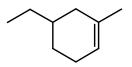
C. (E)-3-cyanohex-3-ene

D. (Z)-3-cyanohex-3-ene

E. (E)-4-cyanohex-3-ene

AB.(Z)-4-cyanohex-3-ene

26.



A. 3-ethyl-1-methylcyclohex-1-ene

B. 1-methyl-3-ethylcyclohex-1-ene

C. 4-ethyl-2-methylcyclohex-1-ene

D. 2-methyl-4-ethylcyclohex-1-ene

E. 5-ethyl-1-methylcyclohex-1-ene

AB 1-methyl-5-ethylcyclohex-1-ene

27.

A. cis-3-methylhex-4-on-2-ene

B. cis-4-methylhex-4-en-3-one

C. cis-3-methylhex-2-en-4-one

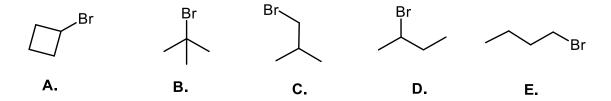
D. *trans*-3-methylhex-4-on-2-ene

E. trans-4-methylhex-4-en-3-one

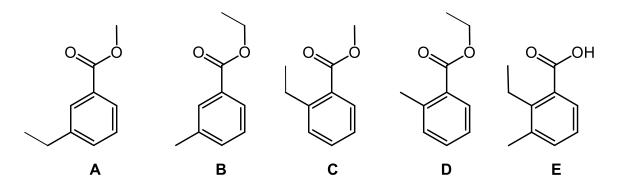
AB.trans-3-methylhex-2-en-4-one

For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

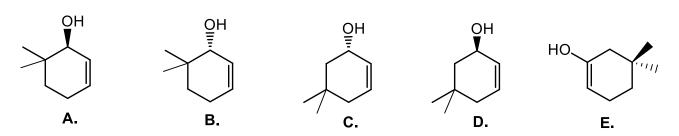
28. sec-butyl bromide



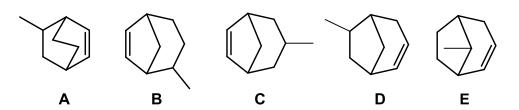
29. ethyl o-methylbenzoate



30. (S)-5,5-dimethylcyclohex-2-en-1-ol



31. 6-methylbicyclo[3.2.1]oct-2-ene:



13% PART 5: STRUCTURE DETERMINATION

Write your answer in the APPROPRIATE BOX on the ANSWER SHEET provided.

Each of the following questions needs to be answered based on compound X which has the molecular formula $C_6H_{10}O$.

- a) Using the information in the periodic table provided, what is the molecular weight of compound X?
- **b**) What is the index of hydrogen deficiency of compound **X**?
- **c**) Identify 3 different oxygen containing functional groups that could be present in isomers of **X**.
- **d**). Draw a line diagram for an isomer of **X** that would have a characteristic IR peak at 1715 cm⁻¹, and contains four types of carbon, and three types of hydrogen.
- e) i Draw a line diagram of an acyclic isomer of X that has a chirality centre. Show the 3D arrangement of the groups at the chirality center using a wedge-hash representation).
 - **ii** On the drawing, assign the Cahn-Ingold-Prelog priority to each of the groups around the chirality center in part **e i** above.
 - iii What is the chirality of the structure you have drawn in part e i above.

13% PART 6: THERMODYNAMICS

Write your answer in the APPROPRIATE BOX on the ANSWER SHEET provided.

Show your calculations in the rough work box as PARTIAL marks may be awarded.

Each of the following questions needs to be answered based on cyclohexane and *trans*-hex-3-ene.

- a) What type of isomers are they?
- b) Write a balanced equation for the combustion of cyclohexane.
- C) One of the isomers **A**, has a heat of combustion (ΔH_C°) = -938 kcal mol⁻¹. The other isomer, **B**, has a heat of formation (ΔH_f°) = -19.3 kcal mol⁻¹. Calculate ΔH_f° , for isomer **A** and ΔH_c° , for isomer **B** using the following heats of combustion: ΔH_C° , C (graphite) = -93.9 kcal mol⁻¹ ΔH_C° , H₂ (gas) = -68.4 kcal mol⁻¹
- d) Draw an energy diagram (with clearly labeled reactants, products, A and B, and all ΔH values for the reactions in part c) to illustrate the relative energy difference between the two isomers.
- e) Identify isomer A and isomer B by drawing their line diagrams.
 STATE whether A or B is more stable and *briefly* justify your choice.

13% PART 7: MECHANISM

Write your answer in the APPROPRIATE BOX on the ANSWER SHEET provided.

(a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the *single reaction sequence* described verbally by the following points in which a carboxylic acid, benzoic acid, is alkylated using isopropyl iodide in the presence of a base, triethylamine, to yield isopropyl benzoate.

Step 1. Deprotonation of benzoic acid by triethylamine to create the conjugate base of benzoic acid (which is a carboxylate ion) and an ammonium ion salt.

Step 2. Attack of the carboxylate ion, as a nucleophile, on the electrophilic carbon of isopropyl iodide producing isopropyl benzoate with the simultaneous loss of an iodide ion as the leaving group.

(b) Draw the structure of another base with a pKa < 12 that could be used to deprotonate benzoic acid for this reaction.

(c) Based on the above sequence, what reagents could be used to synthesize methyl benzoate?

(d) Based on the above sequence, what set of reagents could be used to prepare methoxybenzene from phenol?

(e) Is a phenol more or less acidic than a carboxylic acid? Briefly explain why.

** THE END **

IRH / ASC / F2025

INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm ⁻¹)	<u>WAVELENGTH</u> (μ)	INTENSITY (1)
C-H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
-CH ₃		(bend)	1450 and 1375	6.90 and 7.27	m
-CH ₂	_	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C-C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic a	acid	1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride	e	1800	5.55	s
C-O	Alcohols, Etl	hers, Esters,			
	Carboxylic a	icids	1300-1000	7.69-10.0	s
O-H	Alcohols, Ph	nenols			
	Free		3650-3600	2.74-2.78	m
	H-Bond	ded	3400-3200	2.94-3.12	m
	Carboxylic a	icids (2)	3300-2500	3.03-4.00	m
N-H	Primary and	secondary amines	ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro (R-NO	₂)	1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C-X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, loc	dide	<600	>16.7	s
		· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	 	

⁽¹⁾ s = strong, m = medium and w = weak

⁽²⁾ note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad

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PERIODIC TABLE

1																	18
1A	_																8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3	4											5	6	7	8	9	10
Li	Be											В	C	N	0	F	Ne
6.941	9.012											10.81	12.01	14.01 15	16.00 16	19.00 17	20.18
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
22.99	24.31		7	J	U	,	U		10	11	1,2	26.98	28.09	30.97	32.07	35.45	39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	\mathbf{V}	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.10	40.08	44.96	47.88	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38	69.72	72.59	74.92	78.96	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
85.47	87.62	88.91	91.22	92.91	95.94	(98)	101.1	102.9	106.4	107.9	112.4	114.8	118.7	121.8	127.6	126.9	131.3
55	56	57*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	\mathbf{W}	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.9	137.3	138.9	178.5	180.9	183.9	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209.0	(209)	(210)	(222)
87	88	89**	104	105	106	107	108	109	110	111							
Fr	Ra	Ac	Rf	На	Sg	Ns	Hs	Mt	Uun	Uuu							
(223)	226.0	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)							
											-						

Lanthanides *

Actinides **

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.1	140.9	144.2	(145)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.0	231.0	238.0	237.0	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)