Department of Chemistry
Memorial University
Chemistry 1050
Fall 2016 Final Examination
Time 3 hours

Read the Following Carefully

1. This exam has 14 pages. Question are on pages 2 through 13 and a periodic table is on page 14. Ensure that all pages for the examination paper are present.

2. A sheet containing the periodic table, physical constants and some equations which may be useful to you are provided. The periodic table sheet is the last page of the exam paper **and should be detached for easier use.**

3. **Read each question carefully** and answer each question in the space provided.

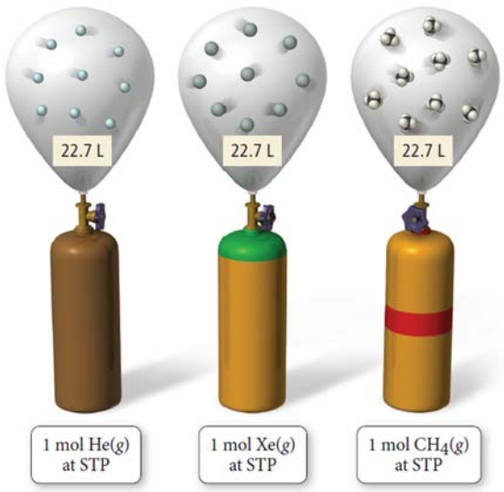
4. Show all relevant calculations.

5. Numerical answers should be reported to the appropriate number of significant digits and MUST include the correct units.

Questions	Points	Grade
1	8	
2-3	9	
4	8	
5-8	11	
9-11	13	
12-13	8	
14-15	6	
16-17	6	
18	6	
19-21	11	
22 - 23	9	
24	4	
total	99	

1. As shown in the figure to the right, one mole of any ideal gas occupies 22.7 L at 273.15 K and at 1 bar, Avogadro's Law.

a) Explain, in terms of the properties of an ideal gas, why the identity of the gas is irrelevant to Avogadro's Law? **(2 marks)**



b) State the conditions of pressure and temperature under which gases exhibit non-ideal behaviour? **(1 mark)**

c) Explain why Xe at STP is the densest gas of those shown in the figure above (ie. compared to both He and CH_4 at STP). **(1 mark)**

d) Compute the density, in g L^{-1}, of Xe at STP. **(2 marks)**

e) The rate of effusion of Xe through a small hole in its container is 0.05 mol hr^{-1}. What would be the effusion rate of He through the same small hole under identical conditions? **(2 marks)**

2. a) You take a bag of potato chips from your air-conditioned car on a summer hike up to the top of The Cabox (a mountain on the west coast of Newfoundland) where it is significantly warmer than your car and the atmospheric pressure is lower. You notice your bag of chips has inflated to the point of bursting. Explain your observation in terms of the kinetic molecular theory of gases. **(2 marks)**

b) Suppose your bag of chips was 2.00 L in your air-conditioned car at 16 ^{o}C and at 101 kPa. At the top of The Cabox, the temperature and pressure are 30 ^{o}C and 91 kPa, respectively. What is the volume of your bag of chips? **(2 marks)**

3. Trinitrotoluene (TNT, $C_7H_5N_3O_6$, MM=227.1311 g mol^{-1}) undergoes complete combustion according to the following balanced chemical equation.

$$C_7H_5N_3O_6(s) + \frac{21}{4}\,O_2(g) \rightarrow 7\,CO_2(g) + \frac{3}{2}\,N_2(g) + \frac{5}{2}\,H_2O(l)$$

If 25.0 g of TNT is combusted in a 450. mL container filled with O_2 to a pressure of 7.00 bar at 298 K, calculate the maximum mass of CO_2 that could be produced? **(5 marks)**

4. a) The decomposition of trinitrotoluene (TNT, $C_7H_5N_3O_6$) was studied in a bomb calorimeter. 6.1891 g of TNT (MM=227.1311 g mol^{-1}) was placed into a bomb calorimeter and was detonated. The temperature of the calorimeter rose from 22.905 to 25.879 ^oC. The heat capacity of the bomb calorimeter was 9.625 kJ $^oC^{-1}$. The decomposition of TNT occurs according to the following reaction. **(5 marks)**

$$C_7H_5N_3O_6(s) \rightarrow \frac{3}{2} N_2(g) + \frac{5}{2} H_2O(l) + \frac{7}{2} CO(g) + \frac{7}{2} C(s, graph)$$

i) Determine $\Delta_r U$ for the decomposition reaction.

ii) Determine $\Delta_r H$ at 298 K for the decomposition reaction.

b) A safer way to determine the enthalpy of reaction of TNT is to use the standard enthalpies of formation of the reactants and products which are provided in the table to the right. Use these values to determine the standard enthalpy of reaction for the decomposition of TNT, the equation for which is given above in part a). **(3 marks)**

Compound	$\Delta_f H^\circ$ / kJ mol^{-1}
$C_7H_5N_3O_6(s)$	-63.2
$H_2O(l)$	-285.83
$CO(g)$	-110.53

5. A 25 g ice cube at 0.0 ^{o}C is dropped into a 250. g cup of hot coffee initially at 97.0 ^{o}C. Assume that coffee has the same heat capacity as water and determine the final temperature of the liquid in the coffee cup. Assume no loss of heat from the system and use data from the data sheet. **(4 marks)**

6. The infrared spectrum of TNT has a strong absorption at a wavelength of 6.631 µm (micrometers) corresponding to N-O stretching. Calculate the frequency corresponding to this wavelength. **(2 marks)**

7. a) Compute the energy change in kJ mol^{-1} corresponding to the n=2 to n=4 transition of an electron in a H atom. **(3 marks)**

b) Would the energy corresponding to the n=2 to n=4 electronic transition be more or less for a He^{+} ion than that calculated above for the H atom? Why? **(1 mark)**

8. Briefly describe in terms of bonds broken and formed, where the energy comes from in an exothermic reaction. **(1 mark)**

9. Explain why the 2s orbital fills before the 2p orbital (i.e. why is the 2s orbital lower in energy than the 2p orbital in a multielectron atom?). You may use a diagram. **(2 marks)**

10. a) Write the **condensed** ground state electron configuration and **condensed** orbital diagram for the following. **(4 marks)**

Species	Condensed electron configuration	Condensed orbital diagram
Example, F	$[He]2s^2 2p^5$	[He] ↑↓ (2s) ↑↓ ↑↓ ↑ (2p)
S		
Ni		
Ni^{2+}		
Sb (element 51)		

11. a) Which period 3 element has the highest electron affinity? **(1 mark)** _____

b) Which group 14 element is the most metallic? **(1 mark)** _____

c) Which period 3 element has the following successive ionization energies? **(1 mark)**
578, 1817, 2745, 11577, 14842, 18379 kJ mol^{-1} _____

d) Write the products for and balance the following equations. **(4 marks)**

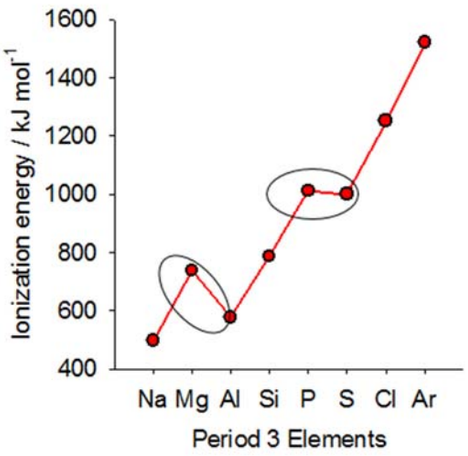
i) $CaO(s) + H_2O(l) \longrightarrow$

ii) $SO_3(s) + H_2O(l) \longrightarrow$

iii) $Na(s) + H_2O(l) \longrightarrow$

iv) $Na(s) + Cl_2(g) \longrightarrow$

12. In general, the ionization energy increases as you go from left to right in the periodic table as shown by the plot of ionization energy vs the period 3 elements. It can also be seen that there are two exceptions to this general trend, going form Mg to Al and from P to S.



a) Why does the ionization energy increase going from left to right in the periodic table? **(1 mark)**

b) Why does Al have a lower ionization energy than Mg? **(1 mark)**

c) Why does S have a lower ionization energy than P? **(1 mark)**

13. Draw the Lewis structure for SO_2 that: **(5 marks)**

a) obeys the octet rule

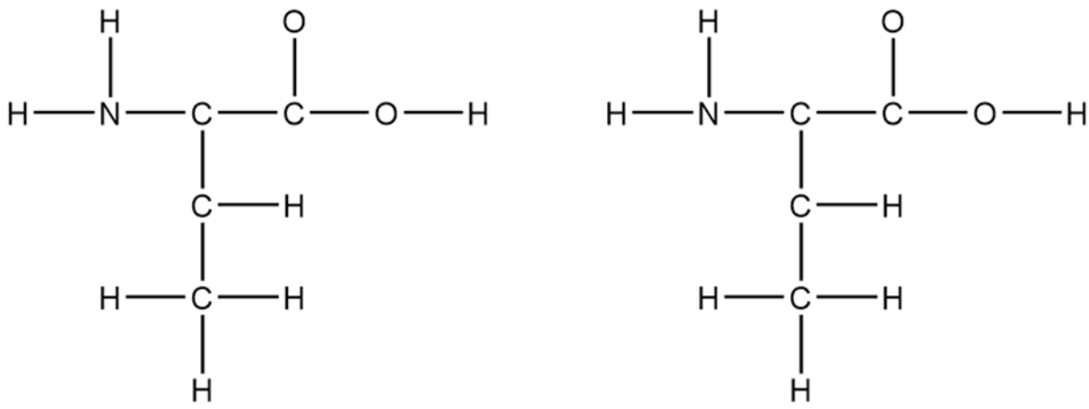
b) reduces the formal charges

c) In your structures above, assign formal charges to each atom.

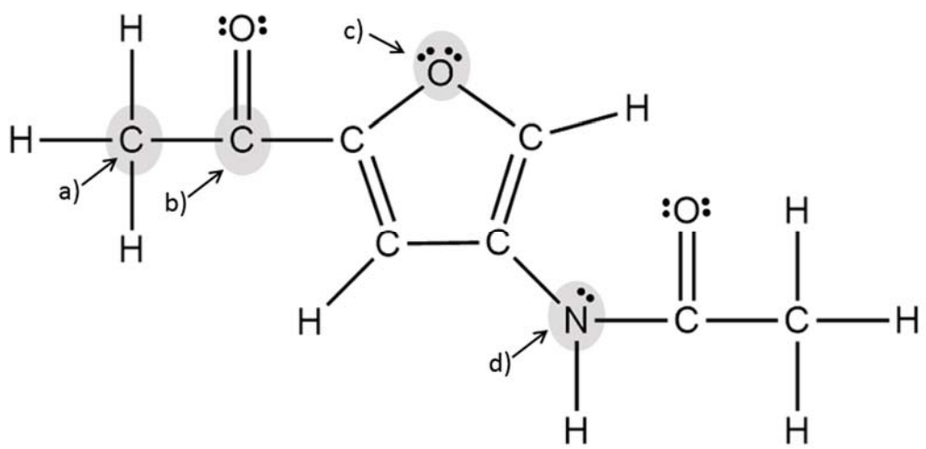
d) Describe the nature of the bonding between S and O in SO_2 (ie. what is the bond order, are the bonds covalent and/or ionic).

e) What is the shape of SO_2? _____

14. Below is a skeletal structure for dehydrobutyrine, $C_4H_7NO_2$, a component of peptide antibiotics. Complete the Lewis structure by filling in lone pairs and multiple bonds where appropriate. There are two structures, one for practice, and one which is final. Circle the one you want marked. Show your work (i.e. counting electrons). **(2 marks)**



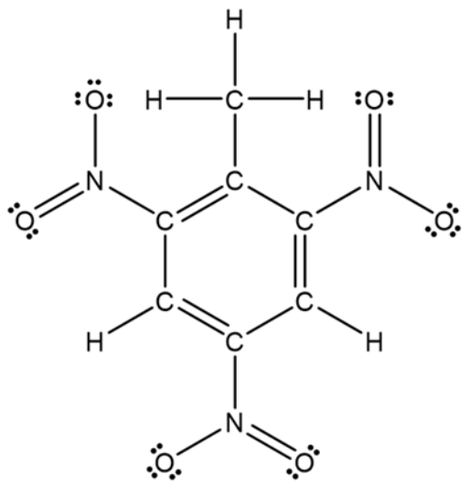
15. Below is the Lewis structure for 3-acetamido-5-acetylfuran (3A5AF). This compound was synthesized in the Chemistry Department at MUN from chitin which is a component of waste crab, lobster, and shrimp shells. (Omari, Dodot, and Kerton *ChemSusChem*, **2012**, *5*, 1767.)



State the molecular geometry and hybridization scheme that accounts for the geometry for each of the highlighted atoms in the structure of 3A5AF, above. **(4 marks)**

Atom	Molecular geometry	hybridization
a)		
b)		
c)		
d)		

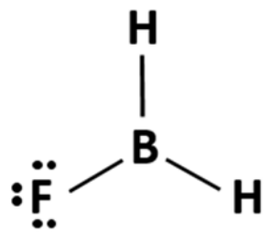
16. The Lewis structure for TNT is shown to the right. Show your work to determine: **(2 marks)**



a) the average bond order between each N and O

b) the average bond order between C atoms in the central ring.

17. The Lewis structure of fluoroborane, BH_2F, is shown to the right. **(4 marks)**



a) Using the Lewis structure, use VSEPR theory to predict the geometry around B.

ii) What is the orbital hybridization around B?

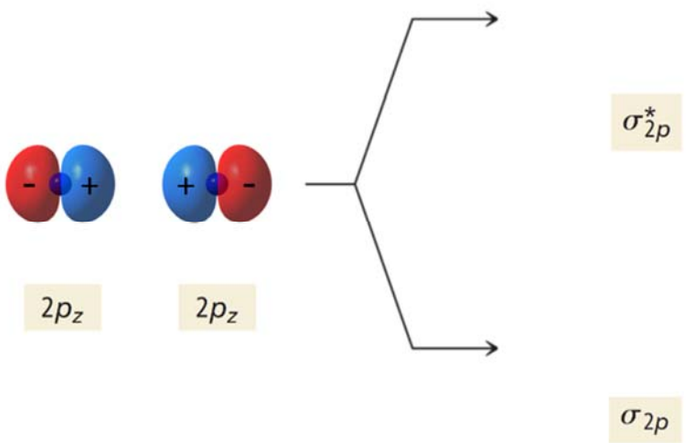
iii) Provide a sketch, illustrating the type of all the bonds in the molecule, sigma (σ) or pi (π), and the atomic or hybrid orbitals that overlap to form these bonds.

18. Sketch the following:

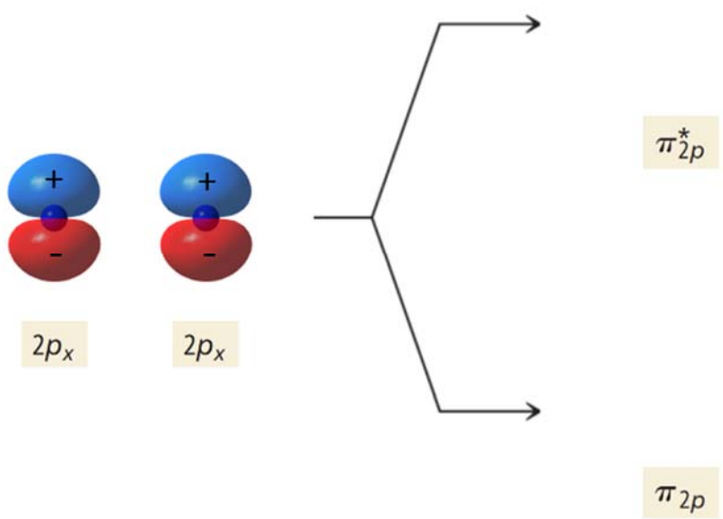
a) an orbital with n=2, l=1 **(1 mark)**

b) an orbital with n=3, l =2 **(1 mark)**

c) the σ_{2p} and σ^*_{2p} molecular orbitals. **(2 marks)**



d) the π_{2p} and π^*_{2p} molecular orbitals. **(2 marks)**



19. a) Draw the molecular orbital diagram for the H_2^- ion. Don't forget to label the atomic and molecular orbitals and populate the MOs with the correct number of electrons. **(2 marks)**

b) What is the bond order for H_2^-? **(1 mark)**

c) What is the bond order for H_2^+? **(1 mark)**

d) Draw the molecular orbital diagram for an excited state of the H_2 molecule and determine its bond order. **(2 marks)**

20. Why is the heat of vaporization of water (40.7 kJ mol^{-1}) significantly higher than the heat of fusion (6.01 kJ mol^{-1})? **(1 mark)**

21. At the summit of The Cabox, a mountain on the west coast of Newfoundland, atmospheric pressure is 91.0 kPa. The normal boiling point of water is 100.0 ^oC (ie. at 101.3 kPa). Calculate the boiling point of water at the summit of the Cabox? Use data from the data page to complete this question. **(4 marks)**

22. Determine whether each of the following compounds is polar. **(6 marks)**

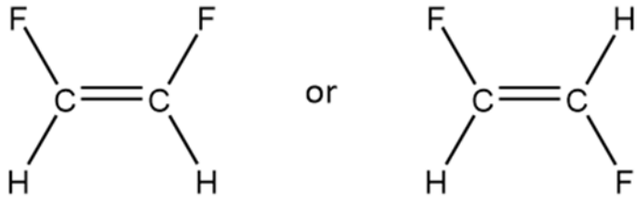
OF_2

SF_4

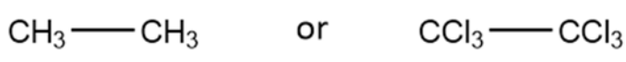
XeF_4

23. Below are skeletal line drawings of pairs of compounds, choose which one is has the highest enthalpy of vaporization (circle) and explain, in terms of intermolecular forces, why you chose it over the other. **(3 marks)**

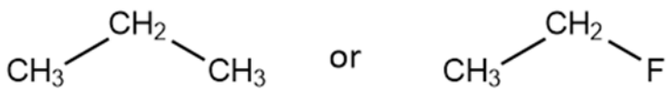
a)



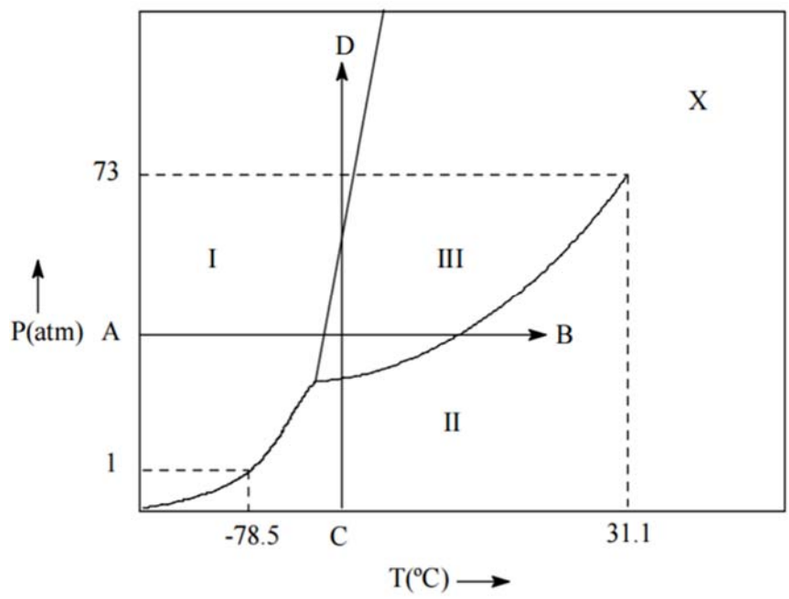
b)



c)



24. Below is the phase diagram for CO_2.



a) Along the isobar, going from A to B, list in order the phase changes that occur. **(1 mark)**

b) Along the isotherm, going from C to D, list in order the phase changes that occur. **(1 mark)**

c) What is the phase that exists at point X on the diagram? **(1 mark)**

d) Clearly mark the triple point on the diagram and label it with a T. Explain the significance of the triple point. **(1 mark)**

1																	18
1 H 1.0079	2											13	14	15	16	17	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	3	4	5	6	7	8	9	10	11	12	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.065	17 Cl 35.453	18 Ar 39.948
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 55.8475	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (99)	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 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.327	57 La 139.9055	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 195.078	79 Au 196.9665	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.9804	84 Po (210)	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 (269)	109 Mt (268)									

atomic mass — 6 C 12.0107 — atomic number

KEY

Lanthanides	58 Ce 140.116	59 Pr 140.9077	60 Nd 144.24	61 Pm (147)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
Actinides	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)

Parenthesis indicates the most stable isotope

Constants

$\Delta_{\text{fus}}H^{\circ}_{\text{H}_2\text{O(s)}} = 6.01 \text{ kJ mol}^{-1}$ at 273 K

$\Delta_{\text{vap}}H^{\circ}_{\text{H}_2\text{O}(l)} = 40.7 \text{ kJ mol}^{-1}$ at 373 K

$\Delta_{\text{vap}}H^{\circ}_{\text{H}_2\text{O}(l)} = 44.0 \text{ kJ mol}^{-1}$ at 298 K

specific heat of $\text{H}_2\text{O}(l) = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$

specific heat of $\text{H}_2\text{O}(s) = 1.960 \text{ J g}^{-1} \text{ K}^{-1}$ at 0 °C

density of $\text{H}_2\text{O}(l)$ near 0 °C = 1.000 g mL^{-1}

$c = 2.998 \times 10^{8} \text{ m s}^{-1}$

$R_H = 1.0973 \times 10^{7} \text{ m}^{-1}$

$h = 6.626 \times 10^{-34} \text{ J s}$

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$= 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$

$F = 9.6485 \times 10^{4} \text{ C mol}^{-1}$

Some Useful Equations

$PV = nRT$ $\qquad E_n(\text{J}) = -2.179 \times 10^{-18} \times \frac{Z^2}{n^2}$

$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$ $\qquad \Delta U = q + w$

$$\Delta E(\text{J}) = -Z^2 \times 2.179 \times 10^{-18} \left(\frac{1}{n_{\text{f}}^2} - \frac{1}{n_{\text{i}}^2}\right)$$

$$\Delta_{\text{r}}H^{\circ} = \Sigma \nu_{\text{p}} \Delta_{\text{f}}H^{\circ}_{\text{products}} - \Sigma \nu_{\text{r}} \Delta_{\text{f}}H^{\circ}_{\text{reactants}}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\Delta_{\text{r}}H = \Delta_{\text{r}}U + \Delta nRT$ $\qquad E_k = \frac{1}{2}m\text{v}^2$

$E_n = h\nu$ $\qquad \lambda\nu = c$

$r_n = \frac{n^2 a_{\text{o}}}{Z^2}$ $\qquad u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ $\qquad \lambda = \frac{h}{m\text{v}}$

Conversion Factors

1 bar L = 100 J

1 atm L = 101.325 J

1 cal = 4.184 J (exactly)

1 L = 1 dm^3

1 mL = 1 cm^3

1 J = 1 kg m^2 s^{-2}

1 bar = 10^5 Pa = 100 kPa = 750.1 torr = 0.9869 atm

Do not turn the paper over until you are told that you may do so.

You may not leave the examination room during the first half hour or during the last half hour of the examination.

At the end of the examination:
When you are told to stop writing you must do so.

ACADEMIC OFFENCES

Academic offences shall be deemed to include, but shall not be limited to, the following:

1. **Cheating on examinations, theses, assignments, work term reports, projects, internship reports, or any other tests.**
   Cheating includes copying from another student's work or allowing another student to copy from one's own work, consulting with any unauthorized person during an examination or test, or using unauthorized aids; or knowingly recording or reporting false empirical or statistical data. The work referred to includes examinations, theses, assignments, work term reports, projects, internship reports, or any other tests which are to be used in judging the student's performance in a course or programme of study, or on any special tests which the University may offer.
2. **Impersonating another student or allowing oneself to be impersonated**.
   By impersonation is meant the imitation of a student or entrance into an arrangement with another person to be impersonated for purposes of taking examinations or tests or carrying out laboratory or other assignments.
3. **Plagiarism.**
   Plagiarism is the act of presenting the ideas or works of another as one's own. This applies to all material such as essays, laboratory reports, work term reports, design projects, seminar presentations, statistical data, computer programmes and research results. The properly acknowledged use of sources is an accepted and important part of scholarship. Use of such material without acknowledgement, however, is contrary to accepted norms of academic behaviour.
4. **Theft of examination papers or other material.**
   By theft is meant obtaining by any improper means examination papers, tests, or any other such material.
5. **Use and/or distribution of stolen material.**
   The use of material which the student knows to have been improperly obtained and/or the distribution of such material is considered to be an academic offence.
6. **Submitting false information**.
   This offence includes falsifying academic forms or records, submitting false credentials, medical or other certificates, or making a false, misleading or incomplete declaration to the University.
7. **Submitting work for one course which has been or is being submitted for another course without express permission to do so.**
   This includes the presentation of an essay, report or assignment to satisfy some or all of the requirements of a course when that essay, report, or assignment has been previously submitted or is concurrently being submitted for another course without the express permission of the professor(s) involved.

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