d) What is the relationship betweennn ion-pair energy and lattice energy ?   1

4. a) With the help of an example show a limitation in predicting structures based on radious ratio calculations.

   b) Although Cu^+ and Na^+ have identical ionic radii, i.e. 96 pm and 95 pm respectively, CuCl has a melting point of 699K while that of NaCl is 1074K. Explain. $1\frac{1}{2} + 1\frac{1}{2}$

5. What are the sailent features of VSEPR? Use it to explain the structure of BrF_3. $1\frac{1}{2} + 1\frac{1}{2}$

6. Deduce the Born-Lande equation for determination of lattice energy of NaCl explaning the term insolved in the derivation.

                                              3

FIRST B.SC. EXAMINATION, 2018

(2nd Semester, Old Syllabus)

CHEMISTRY (SUBSIDIARY)

PAPER - IIIS

Time : Two hours   Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. a) What is the difference between work and energy ? Show by a P-V diagram that the amont of work produced in a two stage isothermal expansion will be different from corresponding single stage expansion operating between same initial and final state.   1+2

   b) What is Joule-Thomson coefficient ? Prove that this coefficient is zero for an ideal gas.   1+3

   c) Explain Hess's law of constant heat summation for a chemical reaction ? Derive the expression that shows the temperature dependence of heat of chemical reaction.

                                                1+3

   d) How can you determine the heat of reaction for the following chemical process, although the direct calorimetric measurement is unsuitable for this coversion?
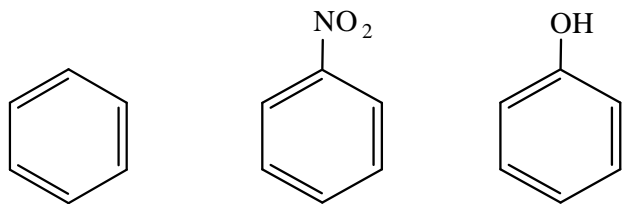
$$2C(s) + O_2(g) \rightarrow 2CO(g)$$ 2

e) For 1 mole of an ideal gas undergoing a reversible polytropic expansion, the relation $PV^n = C$ holds, where n and C are constants with $n > 1$

   i) Calculate work done if the gas expands from V_1 to V_2 (in Litres) with $T_1 = 300K$ and $n = 2$

   ii) If $C_v = 5/2R$, calculate Q, ΔU and ΔH.   4

GROUP - B

2. a) Draw the properly labelled orbital picture of 'benzene' showing hybridisation of each carbon atom. Comment on its shape.   3

b) Comment on the shape and stability of cyclo octatetraene with justification.   3

c) For methyl bromide, the rate of hydrolysis is multiplied more than 5000 by changing the nucleophile from H_2O to $\overset{\ominus}{O}H$; but for t-butyl bromide, the rate is unaffected.— Justify.   3

d) Arrange the following in order of increasing rate of nitration and give your reasons :   3

e) Predict the reagent (s) required for the following reaction. Write down the mechanism of the reaction with properly labelled energy profile diagram.   5
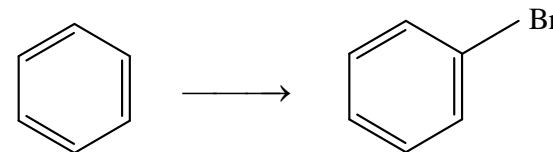
GROUP - C

3. a) Construct the Born Haber cycle for CsCl. Calculate the heat of fromation of CsCl from the following thermochemical data.

$\Delta H_{sub}{}^{Cs} = 78 KJ\, mol^{-1}$; $\Delta H_{IP}{}^{Cs} = 375.7\, KJmol^{-1}$;

$\Delta H_{diss}{}^{Cl_2} = 242\, KJmol^{-1}$; $\Delta H_{EA}{}^{Cl} = -347\, KJmol^{-1}$;

$\Delta H_{lattice}{}^{Cscl} = -661\, KJ\, mol^{-1}$; $2\frac{1}{2}+1$

b) Define "Madelung constant" of an ionic lattice.   2

c) Mention the basic assumptions of radius-ratio calculations for ionic lattices. Using these assumptions, derive the limiting condition for radius ratio of cation to anion having coordination number four in a body centered cubic lattice. $1\frac{1}{2}+2$