(v) Determination of Oxygen in Metal Oxides:

It can be done by dissolution of metal oxides in BrF_3. The metal oxides releases oxygen quantitatively in BrF_3, which is collected and measured by some specific method (like by gas meters). It gives the good test for the direct determination of oxygen e.g.

$$SeO_2 + 2BrF_3 \rightarrow SeF_6 + Br_2 + O_2$$

$$U_2O_5 + 2BrF_3 \rightarrow 2UBrF_2 + OF_2 + 2O_2$$

9/12/2024

7th Semester

6.11 REACTIONS IN MOLTEN SALT SYSTEM (CHEMISTRY OF MOLTEN SALTS)

Introduction:

The chemistry of molten salts as non-aqueous solvents system is one that blossomed in recent years. The most obvious differences when compared with the chemistry of aqueous solutions are anion concentration ↑

- The strongly bonded and stable nature of the solvent.
- A concomitant resistance to destruction of the solvent by vigorous reactions.
- And higher concentration of various species particularly coordinating anions then can be obtained in saturated solution in water

Table 6.9: Melting point, Boiling point and Liquid Range of some fused salts

Salt	Melting point °C	Boiling point °C	Liquid range °C
LiF	845	1680	835
NaF	995	1704	709
NaCl	801	1465	664
KCl	772	1407	635
NaBr	750	1392	642
KBr	735	1383	648
$NaNO_3$	310	Decomposes at 380	–
KNO_3	337	Decomposes	–
NaOH	320	1390	1070
KOH	400	1327	927
Na_2SO_4	890	–	–
K_2SO_4	1069	1689	620
Li_2CO_3	726	Decomposes	–
Na_2CO_3	858	Decomposes	–

Importance: Any salt liquid at room temperature ✓ known as ionic "liquid"

- The chemistry of solutions of molten salts, their equilibria and reactions is of very great technical importance e.g Glass is a super cooled complex.
- Most of the industrial metallurgical processes for the extraction of metals involves the use of high melts to decrease m.p of ore, high m.p solid salts are used.
- The production of volatile products from molten salts system is particularly easy and often extremely conveniently.
- Most salts show sharp increase in conductivity in melting (because ionize). The high conductivities, m.p and large temperature range and solubility of liquids show strong bonding in them. Exception of $HgCl_2$ which has a relatively low equilibrium conductance and a liquid range of only 25 °C indicating that the melt consists of uncharged particle.

Solvent Properties: ✓ They are stable at high temp.

10/12/2024

Classification:

On the basis of a structure of a liquid, molten salts can be conveniently classified into two groups, although there is distinct boundary between the two.

Group-I:

The first consists of compounds such as alkali halides that are bonded chiefly by IONIC FORCES. On melting, very little changes take place in these materials.

1. The coordination of the ions tends to drop from six in the crystals to about four in the melt 6 → 4
2. The longer range order found in the crystal is destroyed, but a local order is still present in which each cation is surrounded by anion.
3. These fused salts are all very GOOD ELECTROLYTES because of the presence of the large number of ions.
4. They behave normally with respect to CRYOSCOPY and is a useful means of study.

technique to use to observe the molecular weight by its freezing point

Group-II:

The second group consists of compounds in which COVALENT BONDING is important. These compounds tend to melt with the formation of discrete molecules, although autoionization may occur e.g, Hg(II) halide ionizes as follows.

$$2HgX_2 \leftrightarrow HgX^+ + HgX_3^-$$

Acidic Basic

oxidation no. changes

And $NO^{3-} \leftrightarrow NO_2^+ + O^{-2}$

$$NO^{3-} + S_2O_7^{2-} \leftrightarrow NO_2^+ + 2SO_4^{2-}$$

In this NO_2^+ is analogous to the H_3O^+ in water. An acidic solution would be formed when oxide acceptors are added to the melt.

Methods for Study of Molten Salt Solutions

1. Cryoscopic method (Depression in freezing point).
2. Phase diagram.
3. Spectroscopic measurements.
4. Electrical conductivities and Transport properties.

(i) Cryoscopic Method (Depression in freezing point method):

If we assure that in dilute solution of salt in a molten salt, solvent o Roult's Law(i.e., in dilute solutions of non volatile, non electrolyte solutes, the pa pressure of solvent in a solution is directly proportional to the mole fraction o solvent) and the solute Henry's Law, one can apply the Van't Hoff relation

$$\Delta T \cong \frac{RT_o^2}{\Delta H_f} \upsilon N_2 = (T_o - T)$$

Where υ = Number of particles produced per formula unit of s (e.g. NaCl $\upsilon = 2$)

N solute= Mole fraction of the solute

ΔH_f = Enthalpy of solvent

T_o= M.P. of pure solvent

ΔT= Observed freezing point depression

Henry's Law: The solubility of a gas in given volume of a liquid at a cons temperature is directly proportional to the pressure of gas above the liquid.

$$X_{solute} = kP_{solute}$$

(ii) Spectroscopic Measurements:

Both vibrational (i.e., IR and electronic (i.e., AAS and UV)). Spectra of mo salt solutions suggest that complex ions are produced in the molten salt syst Addition of KCl to molten $ZnCl_2$ produces two new vibrational frequencies and a moles% KCl the original spectrum of $ZnCl_2$ has disappeared. It seems that [Zn and $[ZnCl_4]^{2-}$ ions are produced. Similar behaviour is found with molten CdCl addition of KCl.

(iii) Electrical Conductivity and Transport Properties:

A distinction between ionic and molecular melts can be made on the basi their conductivity. Most molten chlorides have specific conductivities higher than $^1ohm^{-1}cm^{-1}$ or lower than 10^{-4} ohm^{-1} cm^{-1}. All metal halides have spec conductivities in excess of unity.

If complex ions are formed upon mixing two ionic liquids, then the redu mobility of the complex ion might be expected to reduce the conductivity below that either component.

e.g., In $KCl\text{-}CdCl_2$ melts, the decrease in conductivity has been explained terms of the removal of Cl^- ions to form $[CdCl_4]^{-2}$ and $[CdCl_6]^{-4}$ ions.

Phase Diagram:

Phase diagrams of many simple systems show no compound formation but only either a continuous solid solution or Eutectic formation, e.g., KF-KCl phase diagram shows a simple eutectic formation and KCl-RbCl phase diagram shows solid solution formation.

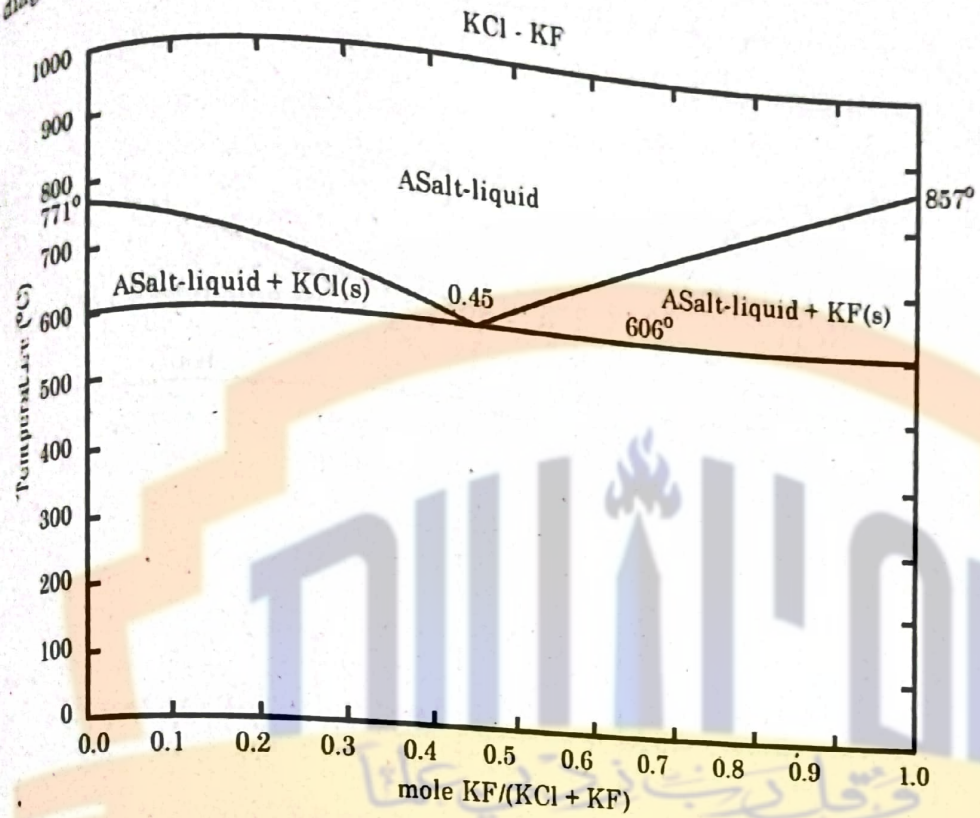

Fig. 6.8: Phase Diagram of KF-KCl system

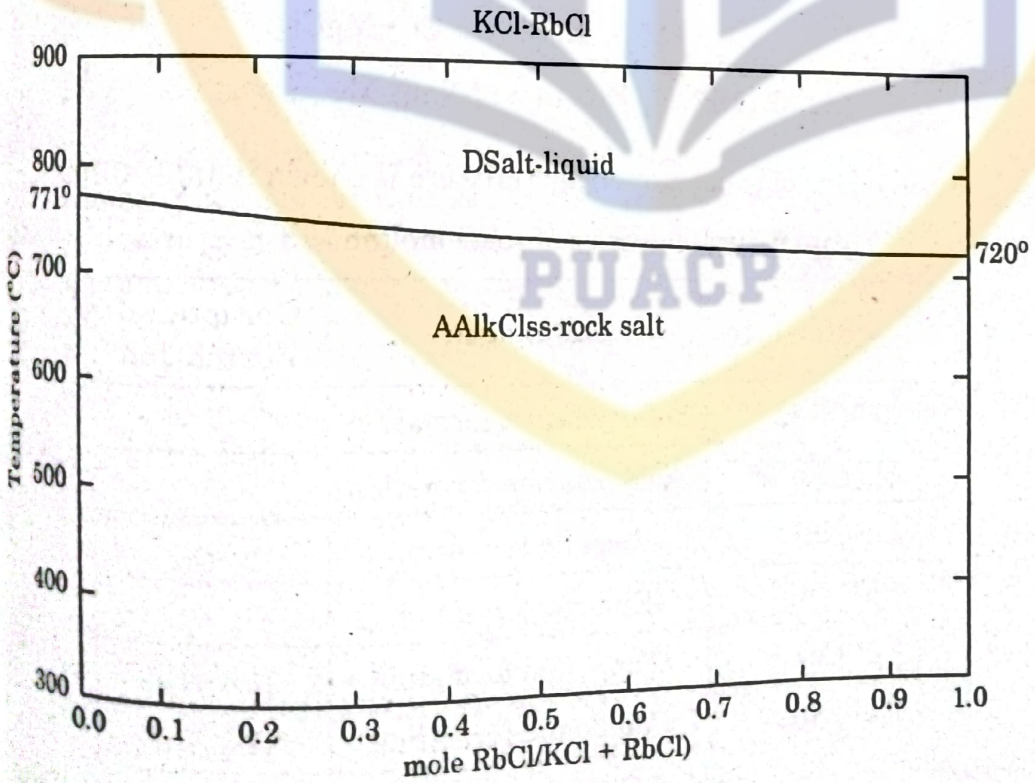

Fig. 6.9: Phase Diagram of KCl-RbCl system.