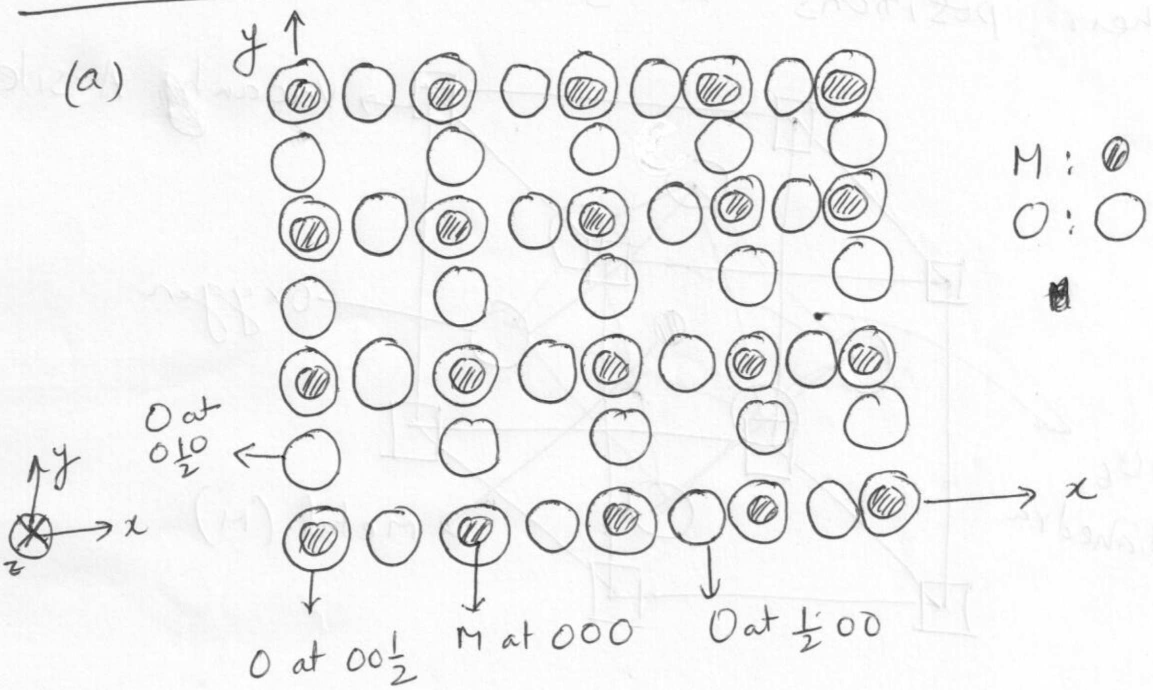
Solution to Problem Set I

NPTEL Course on Electroceramics

Question 1

(a)

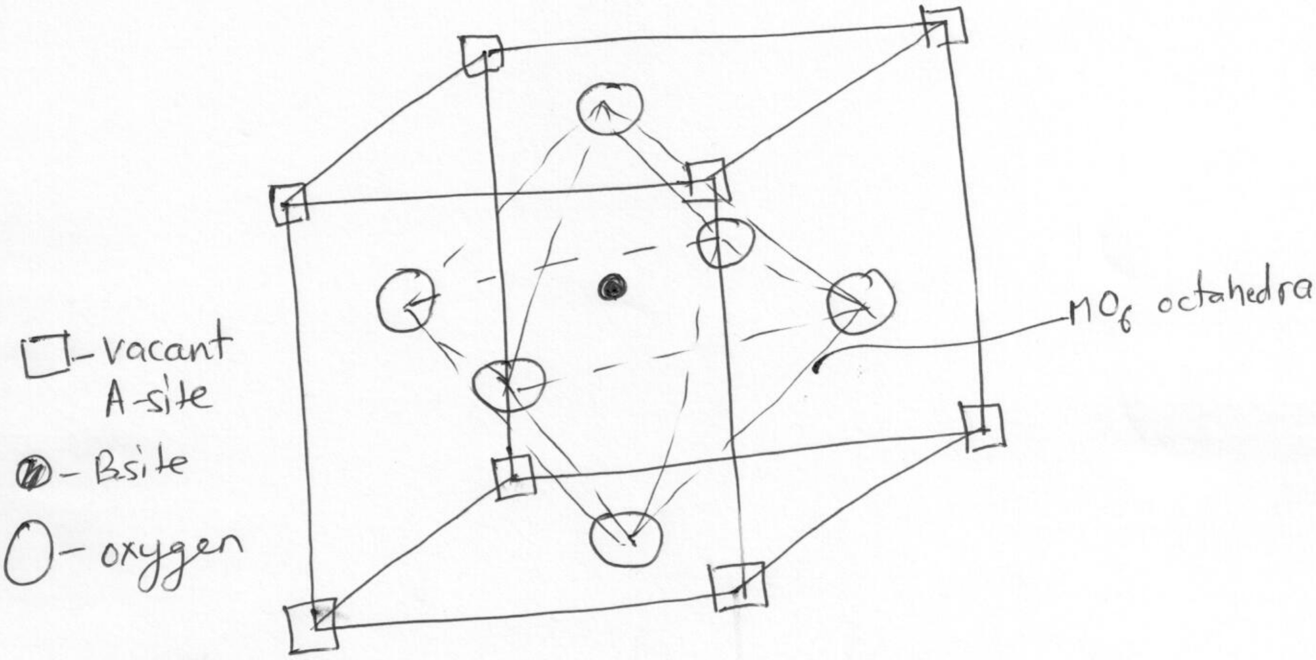


(b) Coordination numbers
Metal (M) is coordinated by six anions (O) → Octahedral
Oxygen (O) is coordinated by two cations (M).

(c) Formula units = MO_3
Each unit cell contains one formula unit.

(d) Lattice type is primitive as there is only one formula unit per unit cell with lattice points at M: 000,
O: $\frac{1}{2}$00
0$\frac{1}{2}$0
00$\frac{1}{2}$

(e) It can be represented as a ABO_3 or perovskite type compound with A atoms missing from their positions as shown below (2)



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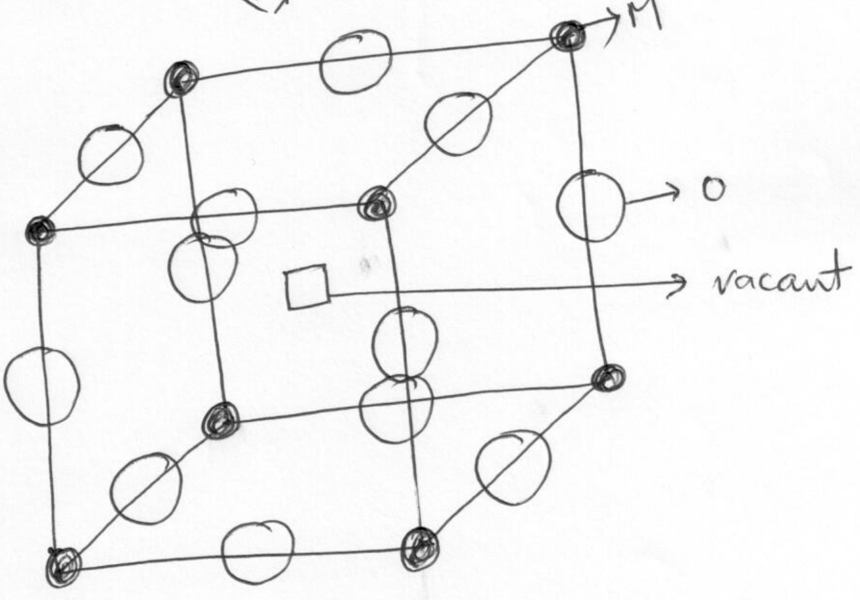
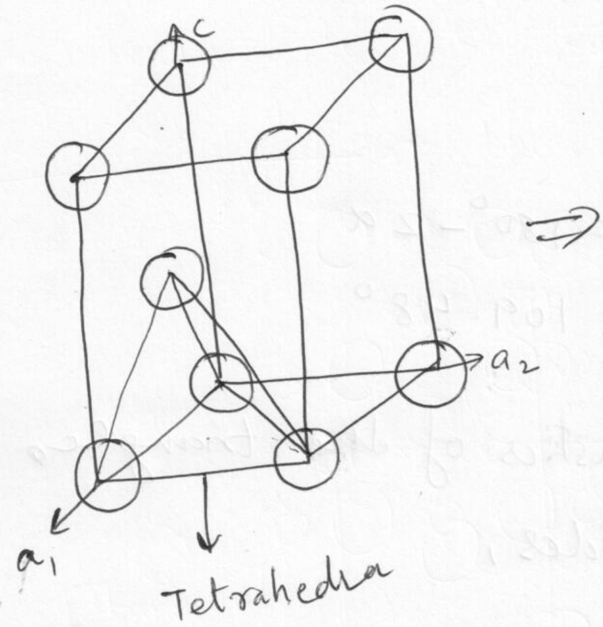
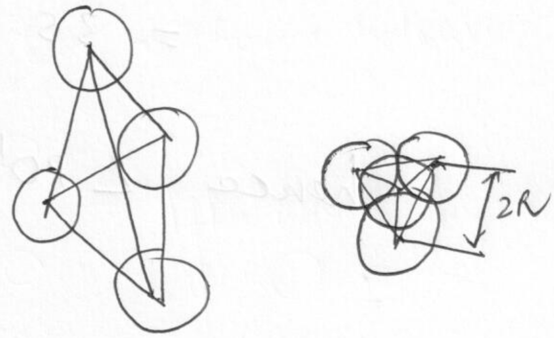


Question (2)

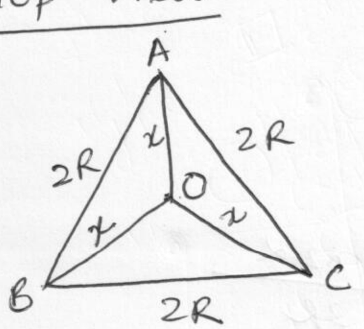




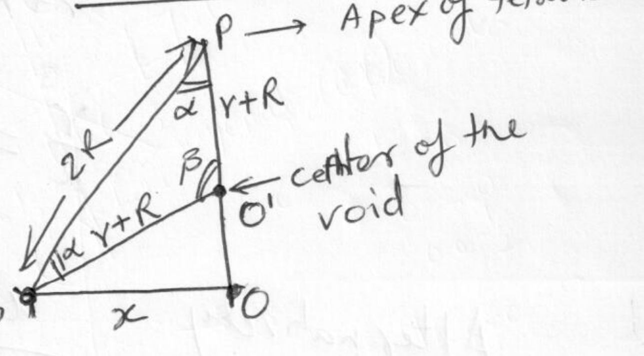
R: Radius of atom

Considering touching sphere model, each side of the tetrahedron is equal to 2R.

Top view



Side view



ABC is the base while O is the projection of the apex of the tetrahedron.

From trigonometry

$$x = \frac{2R \sin 30^\circ}{\sin 120^\circ} = \frac{2}{\sqrt{3}} R$$

Let PO be h which is

$$h = \sqrt{4R^2 - x^2} = \frac{2\sqrt{3}}{\sqrt{3}} R$$

$$\angle PBO' = \alpha = \sin^{-1}\left(\frac{x}{2R}\right)$$

$$= 35.26^{0}$$

Hence $\angle PO'B = \beta = 180^{0} - 2\alpha$

$$= 109.48^{0}$$

By characteristics of the triangle with two equal sides

$$\frac{\sin\alpha}{r+R} = \frac{\sin\beta}{2R}$$

$$\frac{x/2R}{r+R} = \frac{\sin 2\alpha}{2R} = \frac{2\sin\alpha\cos\alpha}{2R}$$

$$\frac{x/2R}{r+R} = \frac{2 \cdot x/2R \cdot h/2R}{2R}$$

$$\frac{1}{R+r} = \frac{h}{2R^2}$$

$$\frac{1}{r+R} = \frac{2\sqrt{2}/\sqrt{3}\,R}{2R^2}$$

$$\boxed{\frac{r}{R} = 0.225}$$

Ques-3

(a) Dissolution of MgO in Al_2O_3

$$2\,MgO \xrightleftharpoons{Al_2O_3} 2\,Mg'_{Al} + 2\,O_O + V_O^{\bullet\bullet}$$ (Ionic compensation)

OR

$$3\,MgO \xrightleftharpoons{Al_2O_3} 2\,Mg'_{Al} + 3\,O_O + Mg_i^{\bullet\bullet}$$

OR

$$\tfrac{1}{2}O_2 + 2\,MgO \xrightleftharpoons{Al_2O_3} 2\,Mg'_{Al} + 3\,O_O + 2\,h^{\bullet}$$ (electronic compensation)

(b) Dissolution of Cr_2O_3 in NiO

$$Cr_2O_3 \xrightleftharpoons{NiO} 2\,Cr^{\bullet}_{Ni} + 2\,O_O + \tfrac{1}{2}O_2\uparrow + 2e'$$ (electronic compensation)

OR

$$Cr_2O_3 \xrightleftharpoons{NiO} 2\,Cr^{\bullet}_{Ni} + 3\,O_O + V''_{Ni}$$ (ionic compensation)

Q.4

TiO_2 Schottky Defect formation

$$\text{null} \rightleftharpoons V_{Ti}^{''''} + 2 V_O^{\bullet\bullet}$$

$$K_s = [V_{Ti}^{''''}] \cdot [V_O^{\bullet\bullet}]^2$$

$$[V_{Ti}^{''''}] \cdot [V_O^{\bullet\bullet}]^2 = \exp\left(-\frac{\Delta H_s}{kT}\right)$$

(assuming no change in entropy).

$$[V_O^{\bullet\bullet}] = 2 [V_{Ti}^{''''}]$$

$$\frac{[V_O^{\bullet\bullet}]^3}{2} = \exp\left(-\frac{\Delta H_s}{kT}\right)$$

$$= \exp\left(-\frac{5.2\ eV \times 1.6 \times 10^{-19}\ C}{1.38 \times 10^{-23}\ J/K \times 1673\ K}\right)$$

$$= 2.24 \times 10^{-16}$$

$$[V_O^{\bullet\bullet}] = 7.65 \times 10^{-6} \text{ mole fraction}$$

$$= \frac{7.65 \times 10^{-6} \times \rho_{TiO_2} \times \text{Avogadro No.}}{M.W._{TiO_2}}$$

$$= \frac{7.65 \times 10^{-6} \times 4 g/cc \times 6.023 \times 10^{23} /mole}{80\ g/mole}$$

$$= 2.30 \times 10^{17}\ cm^{-3}$$

Q.5 $TiO_2 \rightarrow$ oxygen deficient

(a) Defect Reaction

$$Ti_{Ti} + 2O_O \rightleftharpoons Ti_i^{\cdot\cdot\cdot\cdot} + O_2\uparrow + 4e'$$

$$n_e = 4[Ti_i^{\cdot\cdot\cdot\cdot}]$$

$$K_R = pO_2 \cdot [Ti_i^{\cdot\cdot\cdot\cdot}] \cdot n_e^4$$

$$= 256\,[Ti_i^{\cdot\cdot\cdot\cdot}]^5\, pO_2$$

$$[Ti_i^{\cdot\cdot\cdot\cdot}] = \left(\frac{K_R}{256}\right)^{1/5} pO_2^{-1/5}$$

(b) Extent of non stoichiometry

(i) In air, $pO_2 = 0.21\,atm = 0.21 \times 10^{-1}\,MPa$

$$K_R = 6.55 \times 10^{122} \cdot \exp\left[-\frac{960 \times 10^3\, J/mole}{8.315\, J/mol\text{-}K \times 1690\, K}\right] MPa.cm^{-15}$$

$$= 1.39 \times 10^{93}\ MPa \cdot cm^{-15}$$

$$[Ti_i^{\cdot\cdot\cdot\cdot}] = \left(\frac{1.39 \times 10^{93}\, MPa.cm^{-15}}{256}\right)^{1/5} \cdot \left(0.21 \times 10^{-1}\, MPa\right)^{-1/5}$$

$$= 3.038 \times 10^{18}\ cm^{-3}$$

$$= \frac{3.038 \times 10^{18}\ cm^{-3}}{(\text{no. of } TiO_2 \text{ unit per cc})} \quad \text{mole fraction}$$

$$[Ti_i^{\cdot\cdot\cdot\cdot}]_{\text{mole fraction}} = \frac{3.038 \times 10^{18}\ cm^{-3}}{\left(\frac{4\ g/cc \times 6.023 \times 10^{23}\ /mole}{80\ g/mole}\right)}$$

$$= 100\ ppm$$

(ii) at $pO_2 = 10^{-9}\ MPa$

~~$[Ti_i^{\cdot\cdot\cdot\cdot}] = \frac{6.55 \times 10^{122} \cdot \exp(-}{256}$~~

$$[Ti_i^{\cdot\cdot\cdot\cdot}] = \left(\frac{1.39 \times 10^{93}\ MPa\text{-}cm^{-15}}{256}\right)^{1/5} (10^{-9})^{-1/5}$$

$$= 8.85 \times 10^{19}\ cm^{-3}$$

$$= 0.29\ \%$$

(c) Electronic Conductivity $\sigma_e = n e \mu_e$

in air $\sigma_e = n_e(air) \cdot 1.6 \times 10^{-19}\ C \cdot 0.2\ cm^2/V\text{-}s$

$$n_e(air) = 4[Ti_i^{\cdot\cdot\cdot\cdot}] = 4 \times 3.038 \times 10^{18}\ cm^{-3}$$

$$\sigma_e(air) = 4 \times 3.038 \times 10^{18}\ cm^{-3} \times 1.6 \times 10^{-19}\ C \times 0.2\ \frac{cm^2}{V\text{-}s}$$

$$= 0.389\ (\Omega\text{-}cm)^{-1}$$

in 10^{-9} MPa $\sigma_e(10^{-9}\ MPa) = 4 \times 8.85 \times 10^{19}\ cm^{-3} \times 1.6 \times 10^{-19}\ C \times 0.2\ \frac{cm^2}{V\text{-}s}$

$$= 11.328\ (\Omega\text{-}cm)^{-1}$$

Predominantly electronic conductivity due to $[Ti_i^{\cdot\cdot\cdot\cdot}]$ interstitials.

(d) If TiO_2 was stoichiometric, then electronic carrier concn is

$$n_e = n_h = (N_c \cdot N_v)^{\frac{1}{2}} \exp\left(-\frac{E_g}{2k_BT}\right)$$

$$n_e = 2\left(\frac{k_BT}{2\pi \hbar^2}\right)^{\frac{3}{2}} (m_e m_h)^{\frac{3}{4}} \exp\left(-\frac{E_g}{2kT}\right)$$

$$= 2\left(\frac{1.38\times10^{-23}\frac{J}{K} \cdot 1690K}{2\times\pi\times\left(\frac{6.6\times10^{-34}\,J.s}{2\pi}\right)^2}\right)^{\frac{3}{2}} \cdot (9.1\times10^{-31})^{2\times\frac{3}{4}} \exp\left(-\frac{3eV}{kT}\right)$$

$$= 3.38\times10^{26}\ m^{-3} \cdot \exp\left(-\frac{3eV\times1.6\times10^{-19}C}{1.38\times10^{-23}\frac{J}{K} \cdot 1690K}\right)$$

$$= 3.89\times10^{17}\ m^{-3}$$

$$= 3.89\times10^{11}\ cm^{-3}$$

In stoichiometric condition, conductivity would be $\sim10^8$ times lower.

Ques. 6

$NiO - E_g - 4.2\ eV$

$\Delta H_S - 6\ eV$

$D(1000°C) = 1.6 \times 10^{-9}\ cm^2/s$

$\mu_e = \mu_h = 24\ cm^2/V\text{-}s$

$T = 1000°C$

(a) In pure & stoichiometric NiO

Electronic carrier concentration

$$n_e = n_h = (N_C N_V)^{\frac{1}{2}} \exp\left(-\frac{E_g}{2kT}\right)$$

$$(N_C N_V)^{\frac{1}{2}} = 2\left(\frac{k_B T}{2\pi \hbar^2}\right)^{\frac{3}{2}} (m_e \cdot m_h)^{\frac{3}{4}}$$

$$= 2\left(\frac{1.38 \times 10^{-23} J/K \cdot 1273 K}{2\cdot\pi \cdot \left(\frac{6.6 \times 10^{-34} J.s}{2\pi}\right)^2}\right)^{\frac{3}{2}} \cdot (9.1 \times 10^{-31} kg)^{2\cdot\frac{3}{4}}$$

$$= 2.21 \times 10^{26}\ m^{-3}$$

$$n_e = n_h = 2.21 \times 10^{26}\ m^{-3} \cdot \exp\left(-\frac{4.2 eV \times 1.6 \times 10^{-19} C}{1.38 \times 10^{-23} \frac{J}{K} \cdot 1273 K}\right)$$

$$= 5.389 \times 10^{9}\ m^{-3}$$

$$\sigma_{elec} = n_e e \mu_e + n_h e \mu_h = n_e e(\mu_e + \mu_h)$$

$$= 2 \times 5.389 \times 10^{9}\ m^{-3} \times 1.6 \times 10^{-19} C \times \left(24 \times 10^{-4} \frac{m^2}{V\text{-}s}\right)$$

$$= 4.14 \times 10^{-12}\ (\Omega\text{-}m)^{-1}$$

Schottky Defects

$$O = V_{Ni}'' + V_O^{\bullet\bullet}$$

$$\frac{[V_{Ni}'']}{N} = \frac{[V_O^{\bullet\bullet}]}{N} = \exp\left(-\frac{\Delta H_s}{2kT}\right)$$

$$= \exp\left(-\frac{6\,eV \times 1.6\times10^{-19}\,C}{2 \times 1.38\times10^{-23}\,\frac{J}{K} \cdot 1273\,K}\right)$$

$$= 1.36\times10^{-12} \quad \text{mole fraction}$$

$$[V_{Ni}''] = [V_O^{\bullet\bullet}] = 1.36\times10^{-12} \times N \left(\text{no. of NiO formula units per } m^3\right)$$

$$= \frac{1.36\times10^{-12} \times \rho_{NiO}\left(\frac{g}{m^3}\right) \times N_A\left(\frac{1}{mole}\right)}{M.W.\ (g/mole)}$$

$$= \frac{1.36\times10^{-12} \times 6.6\times10^{+6} \times 6.023\times10^{23}}{75}$$

$$= 7.21\times10^{16}\ m^{-3}$$

$$\sigma_{ionic} = \frac{C_{V_O^{\bullet\bullet}} \cdot Z_{V_O^{\bullet\bullet}}^2 \cdot e^2 D_{V_O^{\bullet\bullet}}}{kT}$$

$$= \frac{7.21\times10^{16}\,m^{-3} \cdot (2)^2 \cdot (1.6\times10^{-19}\,C)^2 \cdot 1.6\times10^{-9}\times10^{-4}\,\frac{m^2}{s}}{1.38\times10^{-23}\,\frac{J}{K} \cdot 1273\,K}$$

$$= 6.528\times10^{-30}\ (\Omega\text{-}m)^{-1}$$

$\sigma_{electronic} >> \sigma_{ionic}$

So electronic conduction would dominate

(b) In non-stoichiometric state

$$NiO \longrightarrow Ni_{1-x}O$$

Defect Reaction is

$$\frac{1}{2} O_2 \rightleftharpoons O_O + V_{Ni}'' + 2h^{\bullet} \quad \text{(electronic)}$$

$$\frac{1}{2} O_2 \rightleftharpoons O_O + V_{Ni}'' + 2 Ni_{Ni}^{\bullet} \; (Ni_{Ni}^{2+} \rightarrow Ni_{Ni}^{3+}) \rightarrow \text{(ionic)}$$

V_{Ni}'' ↓ negatively charged; $Ni_{Ni}^{\bullet}$ ↑ positively charged

$$K = \frac{[O_O] \cdot [V_{Ni}''] \cdot [Ni_{Ni}^{\bullet}]^2}{(pO_2)^{\frac{1}{2}}}$$

$$[Ni_{Ni}^{\bullet}] = 2 [V_{Ni}''] \quad , [O_O] = 1$$

$$K = \frac{4 [V_{Ni}'']^3}{(pO_2)^{\frac{1}{2}}}$$

(c) Conductivity will be of p-type by migration of holes. ~~Ba~~

since n_h or $V_{Ni} \propto pO_2^{\frac{1}{6}}$

$$\sigma_{ionic} \propto (pO_2)^{\frac{1}{6}}$$

Ques. 7

$C_{K^+} = 4.07 \times 10^{27}\ m^{-3}$

At 573 K, $\sigma_{total}^{573K} = 1.53 \times 10^{-2}\ S/m$

$D(K^+)_{573K} = 1.89 \times 10^{-14}\ m^2/s$

$$\sigma_{ionic}^{573K} = \frac{C_{K^+}\, Z_{K^+}^2\, e^2\, D_{K^+}}{RT}$$

$$= \frac{(4.07 \times 10^{27} m^{-3}) \cdot (1)^2 \cdot (1.6 \times 10^{-19} C)^2 \cdot (1.89 \times 10^{-14} m^2/s)}{1.38 \times 10^{-23}\ J/K \cdot 573\ K}$$

$$= 2.49 \times 10^{-4}\ S/m$$

Ionic transport no.

$$t_i^{573K} = \frac{\sigma_{ionic}^{573K}}{\sigma_{total}^{573K}} = \frac{2.49 \times 10^{-4}}{1.53 \times 10^{-2}} = 0.016$$

$\Delta H_D (K^+) = 23\ kJ/mole$

$$D_{K^+} = D_0 \cdot \exp\left(-\frac{\Delta H_D^{K^+}}{RT}\right)$$

For two different temperatures T_1 & T_2

$$D_{T_1} = D_{T_2} \cdot \exp\left(-\frac{\Delta H_D^{K^+}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$D_{K^+}^{298K} = D_{K^+}^{573K} \exp\left(-\frac{23 \times 10^3 \frac{J}{mol}}{8.31 \frac{J}{mol \cdot K}}\left(\frac{1}{573K} - \frac{1}{298K}\right)\right)$$

$$\doteq 2.19 \times 10^{-16}\ m^2/s$$

Correspondingly

$$\sigma_{ionic}^{298K} = 5.5 \times 10^{-6}\ S/m$$