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Thermodynamic activity of cuprous-cupric redox oxides in alkali copper silicate glasses

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Thermodynamic activity of cuprous-cupric redox oxides was studied systematically by equilibrating Cu^+-Cu^{2+} redox in alkali copper silicate glasses with varying CuO concentration from 1.0–3.0 mol% at 1200°C, 1300°C and 1400°C in air as furnace atmosphere. The relation between $\log[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ and mol% CuO concentrations, $\log[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ versus temperature as well as $\log[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ versus glass composition were established. The ratio of the logarithm of $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ was found to decrease with decreasing alkali oxides concentrations and increasing mol% CuO in glasses at a constant temperature in air. Further, the logarithmic ratio of $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ was observed to decrease with increasing temperature in the glass of a constant composition. Negative deviations in the logarithm of the activities ratio of oxides of copper from Raoultian behaviour was observed in the molten glass solutions containing up to 1.0–3.0 mol% CuO at constant temperature. The results obtained were explained thermodynamically. Structural considerations in glasses containing Cu^+ and Cu^{2+} ions were also found to play an important role in determining the oxidation-reduction equilibrium along with Cu^+-Cu^{2+} redox reaction. The process of partial molar mixing of oxides of copper in alkali copper silicate glasses at high temperatures was found to be endothermic, apart from main band at 787 nm due to Cu^{2+} ion centred at around 1390 nm in near infra red region in sodium aluminoborate glasses.

Earlier, it was believed that Cu^{2+} ion was a weak colorant [1] but later on it was observed that intense blue colour could be obtained by melting glasses with copper under oxidising conditions [2]. Singh and Kumar [3] studied systematically the optical absorption characteristics of cupric ion in binary alkali silicate glasses containing lithia, soda and potash as well as ternary soda lime silica glasses. The absorption band in the visible region was found to shift more towards longer wavelength on molar replacement of one alkali oxide by another with increasing ionic radii of alkali ions in the order of $K^+ > Na^+ > Li^+$ in the same series of 30 R_2O. 70SiO_2 ($R^+ = Li^+$, Na^+ and K^+ ions) glass. The authors [3] calculated the molar extinction coefficients of cupric ion in their silicate glasses and reported the intensities of the visible bands quantitatively in the order of 10^2 $gm \cdot mol \cdot lit^{-1} \cdot cm^{-1}$. Since, the electronic transition was d-d spin allowed from $^2E_g \rightarrow {}^2T_g$ energy level as mentioned earlier by Bamford [4], Kumar [5] and Bates [6] due to single unpaired electron in Cu^{2+} ion with distorted octahedral symmetry as such Singh and Kumar [3] believed that cupric copper was a strong colorant in the silicate glass. However, the UV-optical absorption characteristics of Cu^+ ion and the mechanism of charge transfer in a sodium silicate glass has been detailed already. Dwivedi and Nath [7] had suggested the mechanism of red colour formation due to colloidal copper particles in copper ruby glasses.

The ESR studies [8, 9] on Cu^{2+} ion in borate glasses and silicate gels have revealed that cupric ion is present in distorted octahedral symmetry in the glass as well as it is a part of silicate network in the silica gel. Darab and MacCrone [8] have investigated the room temperature EPR spectra of silicate gels containing cupric complexes calcined at various temperatures and reported that the major chemical and structural changes occur with increasing calcining temperature in the silica network. Further, the authors mentioned that the cupric complexes incorporated in the gels were extremely stable retaining their inner sphere legation surrounding even after calcining in the temperature range of 50–446°C.

Several earlier investigators have studied the Cu^+-Cu^{2+} and Cu^0-Cu^+ redox reactions in glasses at different temperatures and partial pressures of oxygen. Singh *et al.* [10] studied the kinetics of Cu^+-Cu^{2+} redox reaction in a sodium aluminoborate glass at different temperatures in air as furnace atmosphere. They suggested the mechanism of peroxide ion formation in the glass and reported that the Cu^+-Cu^{2+} redox reaction has obeyed the first order kinetics in the glass. Further, the authors found that the rate constant for the reaction had decreased with increasing temperature in the glass and it did not favour the Arrhenius law. The decrease in the rate constant for Cu^+-Cu^{2+} redox reaction with increasing temperature was attributed due to the change in stable state of Cu^+ ($3d^{10}$) ion to a metastable state of Cu^{2+} ($3d^9$) ion in the glass. Since, the change in enthalpy for the reaction was calculated as

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−12.5 kcal/mole by the authors [10] as such they reported the Cu^+-Cu^{2+} redox equilibrium as exothermic reaction in the glass. Banerjee and Paul [11] studied the thermodynamics of Cu^+-Cu^{2+} redox reaction in a borate glass at different temperatures in air and they also mentioned that the equilibrium reaction was exothermic as the enthalpy change for the reaction was negative. Further, the authors also studied the Cu^o-Cu^+ redox reaction in a low melting borate glass with varying partial pressure of oxygen from 10^{-12} to 10^{-17} atmosphere. The melt was equilibrated for Cu^o-Cu^+ redox in contact with metallic copper crucible under strongly reducing atmosphere to produce a ruby colour in the molten glass. During their investigations they found that the best ruby was formed in the glass at 10^{-14} atmosphere reduced partial pressure of oxygen. Cable and Xiang [12] also studied the Cu^+-Cu^{2+} redox equilibrium in a soda-lime-silica glass at different temperatures in air and calculated the enthalpy change for the equilibrium reaction as 36.84 cal/mol from the slope of the curve obtained on plotting log (Cu^+/Cu^{2+}) versus reciprocal of temperature. The authors mentioned that the rate of approach of equilibrium was faster in stirred melts than static. Cable and Xiang [13, 12] developed an useful model for calculating the molar extinction coefficient of cupric ion in a 17.6 Na_2O-12.0 CaO-70.4 SiO_2 glass which had involved three slopes of the straight lines obtained for absorbance maxima due to Cu^{2+} ion versus total copper concentration relation during Cu^+-Cu^{2+} redox equilibrium investigated at three different temperatures in the glass. The derivation of their model was based on the fact that Cu^+:Cu^{2+} ratio was independent of the total copper concentration over the range of 0.10–1.20 mol% CuO.

Johnston and Chelko [14] studied the Cu^+-Cu^{2+} redox equilibrium in a sodium disilicate glass on varying partial pressure of oxygen at a constant temperature and reported that the redox equilibrium shifted more towards the cupric state with increasing partial pressure of oxygen. Further, they also investigated the effect of pO_2 on Cu^o-Cu^+ redox equilibrium in the silicate glass and mentioned that the solubility or precipitation of copper in the molten glass at a particular temperature was dependent only upon the partial pressure of oxygen in the furnace atmosphere above the melt.

Singh and Kumar [15] had investigated the effect of glass composition on Cu^+-Cu^{2+} redox equilibrium in binary alkali silicate glasses at a constant temperature at 1400°C in air. The Cu^+-Cu^{2+} redox equilibrium shifted more towards oxidised state with increasing alkali concentration or increasing ionic radii of alkali ions in binary silicate glasses. They obtained three concurrent straight lines on plotting log $K'[K' = (Cu^{2+})/(Cu^+)(pO_2)^{1/4}]$ versus mol% alkali oxides for binary alkali silicate glasses. The slopes of their curves were inversely proportional to the coulombic force between alkali ions and non-bridging oxygens in the glass. Since, the oxygen ion activity increases with increasing basicity of the glass, the Cu^+-Cu^{2+} redox equilibrium was found by the authors [15] to shift more towards cupric state. Similar results were also observed by earlier workers [16–20] in binary silicate glasses where the redox equilibria such as Cr^{3+}-Cr^{6+}, Fe^{2+}-Fe^{3+}, Ce^{3+}-Ce^{4+}, As^{3+}-As^{5+} and Sn^{2+}-Sn^{4+} were found to shift more towards oxidised states with increasing basicities of the glass at a constant temperature in air atmosphere.

After an extensive literature survey it was found that the kinetics and thermodynamics of Cu^+-Cu^{2+} redox equilibrium reaction had been studied at high temperatures in glasses containing minor quantities of copper oxide which did not influence the melt composition. When the glass is melted with the major quantities of copper oxide then it is expected to influence the molten glass composition significantly as such the activity coefficients of oxides of copper may play their vital role during the cuprous—cupric redox processes. Keeping in view the lack of thermodynamic activity of cuprous—cupric redox oxides at high temperatures in glasses, the present investigation was undertaken in alkali copper silicate glasses.

1. Experimental

Homogeneous mixture of glass batches having composition $(30R_2O \cdot 70SiO_2)_{1-x}$ $(CuO)_x$ [Where, $R^+ = Li^+$, Na^+ and K^+ ions and x is an integer] were prepared with properly weighed acid washed quartz, AnalaR grade alkali carbonates and cupric oxide. Alkali silicate glasses containing 1.0–3.0 mol% CuO were melted in a 100 ml capacity alumina crucible kept in an electric globar rod furnace for four hours at 1400°C in air atmosphere. The temperature of the furnace was controlled by an automatic temperature indicator-cum-controller within ±5°C connected with R-type Pt-13% Rh/Pt thermocouple. After melting the glasses were cast and poured onto an iron sheet. The glasses were cooled, crushed and remelted for a period of an another two hours in the furnace at the same temperature to ensure homogeneity. Further, the molten glasses were taken out of the furnace and poured onto an iron sheet. After cooling and crushing the glass samples were stored in a desiccator. 15 gms portions of each glass samples in duplicate were heat-treated in 30 ml alumina crucibles kept in the globar rod furnace at 1200°C, 1300°C and 1400°C temperature in air atmosphere for equilibrating Cu^+-Cu^{2+} redox in the glass. After heat treating the glass samples for different lengths of time they were taken out the furnace and poured onto an iron sheet. The glasses were cooled, crushed and stored in a desiccator for spectrocolorimetric chemical analysis of Cu^+, Cu^{2+} ions and total copper. The concentrations of cuprous, cupric and total copper as cupric ion separately in the glass were determined without disturbing Cu^+:Cu^{2+} ratio using iodine monochloride and sodium diethyl dithiocarbamate methods.

When the concentrations of cuprous copper and total copper as cupric did not change with the duration of heat treatment at a particular temperature within an experimental error of ±5% then it was concluded that the equilibrium between both the valence states of copper had been established in a particular alkali copper silicate glass.

TABLE I Equilibrium solubility of copper oxide and logarithm of activity coefficients ratio for oxides of copper in alkali copper silicate glasses at different temperatures in air atmosphere

			Concentration in wt% at different temperatures									$\log \frac{[\gamma_{CuO}]^2}{[\gamma_{Cu_2O}]}$ at different temperatures		
			1200°C			1300°C			1400°C					
S. no.	Glass composition (mol%)	Heat treatment time (hrs)	ΣCu	Cu^+	$Cu^{2+} = \Sigma Cu\text{-}Cu^+$	ΣCu	Cu^+	$Cu^{2+} = \Sigma Cu\text{-}Cu^+$	ΣCu	Cu^+	$Cu^{2+} = \Sigma Cu\text{-}Cu^+$	1200°C	1300°C	*1400°C
L_1	$(29.7Li_2O \cdot 69.3SiO_2)(1.0CuO)$	13	1.083	0.900	0.183	1.490	0.813	0.677	0.813	0.531	0.282	−0.038	−0.636	−1.150
L_1	$(29.7Li_2O \cdot 69.3SiO_2)(1.0CuO)$	16	1.083	0.900	0.183	1.490	0.813	0.677	0.813	0.531	0.282	−0.038	−0.636	−1.150
L_2	$(29.4Li_2O \cdot 68.6SiO_2)(2.0CuO)$	13	2.164	1.186	0.978	2.975	1.106	1.869	1.625	1.012	0.613	−1.374	−1.384	−1.544
L_2	$(29.4Li_2O \cdot 68.6SiO_2)(2.0CuO)$	16	2.164	1.186	0.978	2.975	1.106	1.869	1.625	1.012	0.613	−1.374	−1.384	−1.544
L_3	$(29.25Li_2O \cdot 68.25SiO_2)(2.5CuO)$	13	2.708	1.605	1.103	3.715	1.487	2.228	2.033	1.253	0.780	−1.347	−1.408	−1.661
L_3	$(29.25Li_2O \cdot 68.25SiO_2)(2.5CuO)$	16	2.708	1.605	1.103	3.715	1.487	2.228	2.033	1.253	0.780	−1.347	−1.408	−1.661
L_4	$(29.1Li_2O \cdot 67.9SiO_2)(3.0CuO)$	13	3.250	2.175	1.075	4.475	2.000	2.475	2.407	1.625	0.782	−1.193	−1.371	−1.550
L_4	$(29.1Li_2O \cdot 67.9SiO_2)(3.0CuO)$	16	3.250	2.175	1.075	4.475	2.000	2.475	2.407	1.625	0.782	−1.193	−1.371	−1.550
N_1	$(29.7Na_2O \cdot 69.3SiO_2)(1.0CuO)$	13	1.165	0.657	0.508	1.084	0.680	0.403	1.182	0.760	0.422	−0.479	−0.845	−1.345
N_1	$(29.7Na_2O \cdot 69.3SiO_2)(1.0CuO)$	16	1.165	0.657	0.508	1.084	0.680	0.403	1.182	0.760	0.422	−0.479	−0.845	−1.345
N_2	$(29.4Na_2O \cdot 68.6SiO_2)(2.0CuO)$	13	2.330	1.146	1.184	2.164	1.267	0.897	2.363	1.427	0.936	−0.972	−1.270	−1.763
N_2	$(29.4Na_2O \cdot 68.6SiO_2)(2.0CuO)$	16	2.330	1.146	1.184	2.164	1.267	0.897	2.363	1.427	0.936	−0.972	−1.270	−1.763
N_3	$(29.25Na_2O \cdot 68.25SiO_2)(2.5CuO)$	13	2.912	1.584	1.328	2.708	1.640	1.068	2.950	1.879	1.071	−0.931	−1.310	−1.760
N_3	$(29.25Na_2O \cdot 68.25SiO_2)(2.5CuO)$	16	2.912	1.584	1.328	2.708	1.640	1.068	2.950	1.879	1.071	−0.931	−1.310	−1.760
N_4	$(29.1Na_2O \cdot 67.9SiO_2)(3.0CuO)$	13	3.485	1.702	1.783	3.250	1.833	1.417	3.500	2.300	1.200	−1.156	−1.507	−1.769
N_4	$(29.1Na_2O \cdot 67.9SiO_2)(3.0CuO)$	16	3.485	1.702	1.783	3.250	1.833	1.417	3.500	2.300	1.200	−1.156	−1.507	−1.769
K_1	$(29.7K_2O \cdot 69.3SiO_2)(1.0CuO)$	13	0.842	0.627	0.215	1.084	0.710	0.374	0.906	0.500	0.406	+0.248	−0.762	−1.493
K_1	$(29.7K_2O \cdot 69.3SiO_2)(1.0CuO)$	16	0.842	0.627	0.215	1.084	0.710	0.374	0.906	0.500	0.406	+0.248	−0.762	−1.493
K_2	$(29.4K_2O \cdot 68.6SiO_2)(2.0CuO)$	13	1.672	1.213	0.459	2.164	1.320	0.844	1.810	0.934	0.876	−0.124	−1.199	−1.890
K_2	$(29.4K_2O \cdot 68.6SiO_2)(2.0CuO)$	16	1.672	1.213	0.459	2.164	1.320	0.844	1.810	0.934	0.876	−0.124	−1.199	−1.890
K_3	$(29.25K_2O \cdot 68.25SiO_2)(2.5CuO)$	13	2.093	1.480	0.613	2.708	1.693	1.015	2.258	1.149	1.109	−0.289	−1.252	−2.004
K_3	$(29.25K_2O \cdot 68.25SiO_2)(2.5CuO)$	16	2.093	1.480	0.613	2.708	1.693	1.015	2.258	1.149	1.109	−0.289	−1.252	−2.004
K_4	$(29.1K_2O \cdot 67.9SiO_2)(3.0CuO)$	13	2.510	1.678	0.832	3.250	1.902	1.348	2.685	1.188	1.497	−0.500	−1.447	−2.250
K_4	$(29.1K_2O \cdot 67.9SiO_2)(3.0CuO)$	16	2.510	1.678	0.832	3.250	1.902	1.348	2.685	1.188	1.497	−0.500	−1.447	−2.250

*The value obtained by extrapolation of the curve plotted for standard change in free energy (ΔG^o) vs temperature.

2. Results and discussion

Results presented in Table I show the equilibrium solubility of copper oxide in alkali copper silicate glasses. The relation between log $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ and mol% total copper concentration as CuO at different temperatures in alkali copper silicate glasses containing lithia, soda and potash has been shown in Table I and Figs 1–3. Since, the present alkali copper silicate glasses dissolve appreciable amount of CuO during their preparation as such the glass composition and its structure are expected to be greatly influenced. During the glass preparation process in normal melting conditions in air as both the valency states of copper such as Cu^+ and Cu^{2+} ions are present in large quantities, the following oxide Equation 1 has been used in preceding discussion to represent the cuprous—cupric redox equilibrium reaction in glasses.

$$Cu_2O + \frac{1}{2}O_2 \overset{\Delta G^{\circ}}{\rightleftharpoons} 2CuO \qquad (1)$$

The following Ellingham's Equation 2 and van't Hoff reaction isotherm (3) were used in order to calculate the ratio of the activities of Cu_2O and CuO in glasses at high temperatures.

$$\Delta G^{\circ} = \mathrm{A} + \mathrm{BT}\log T + \mathrm{CT} \qquad (2)$$

and

$$\Delta G = \Delta G^{\circ} + \mathrm{RT}\ln K \qquad (3)$$

where, K is the equilibrium constant and ΔG is the free energy change for the reaction (1) at a particular temperature and constant partial pressure of oxygen. A, B and C are constants for the reaction. The value of K can be given in terms of activities of Cu_2O and CuO as follows:

$$K = \frac{(a_{CuO})^2}{(a_{Cu_2O})(\mathrm{pO}_2)^{1/2}} \qquad (4)$$

According to thermodynamic condition of equilibrium for the reaction (1)

$$(\Delta G)_{T,\mathrm{P}} = 0 \qquad (5)$$

So, the Equation 3 becomes 6 as given below:

$$\Delta G^{\circ} = -\mathrm{RT}\ln K \qquad (6)$$

The logarithmic ratio of the activity coefficients of cuprous oxide and cupric oxide at constant temperature can be calculated using the following Equations 7 and 8:

$$a_{Cu_2O} = \gamma_{Cu_2O} \cdot \mathrm{C}_{Cu_2O} \qquad (7)$$

and

$$a_{CuO} = \gamma_{CuO} \cdot \mathrm{C}_{CuO} \qquad (8)$$

where, γ_{Cu_2O} and γ_{CuO} are the activity coefficients of cuprous and cupric oxides in glasses, respectively. The C_{Cu_2O} and C_{CuO} are the concentrations of Cu_2O and CuO in glasses.

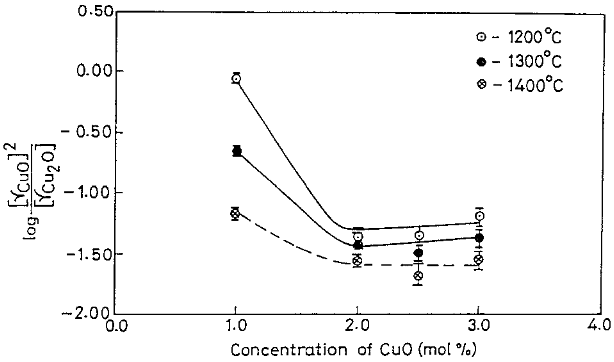

Figure 1 Variation of the log $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ for Cu^+-Cu^{2+} redox equilibrium with mol% total copper as CuO in a $(30Li_2O \cdot 70SiO_2)_{1-x}$ $(CuO)_x$ glass at different temperatures.

The relation of log $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ with mol% CuO concentration as given in Fig. 1 at a particular temperature shows a constancy with decreasing concentration of CuO from 3.0–2.0 mol% CuO which is indicative of its Henry's law behaviour within this range. Further, a decreasing in CuO concentration causes a deviation from its Henarian behaviour and the solution of copper oxide in the lithium silicate glass approaches Raoultian behaviour at a particular temperature as the logarithmic ratio of $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ tends towards unity. The value of log $[\gamma_{CuO}]^2/[\gamma_{CuO}]$ was found to increase with decreasing mol% CuO concentration or increasing mol% alkali oxide concentration at a constant temperature in the present series of alkali silicate glasses containing Li_2O, Na_2O and K_2O as shown in Figs 1–3 which dictates that the Cu^+-Cu^{2+} redox equilibrium shifts more towards the oxidised state with increasing basicity of the glass. Since, the oxygen ion activity increases with increasing basicity of the glass as pointed out by earlier workers [21–24] as such the role played by oxygen ion activity of glass on Cu^+-Cu^{2+} redox

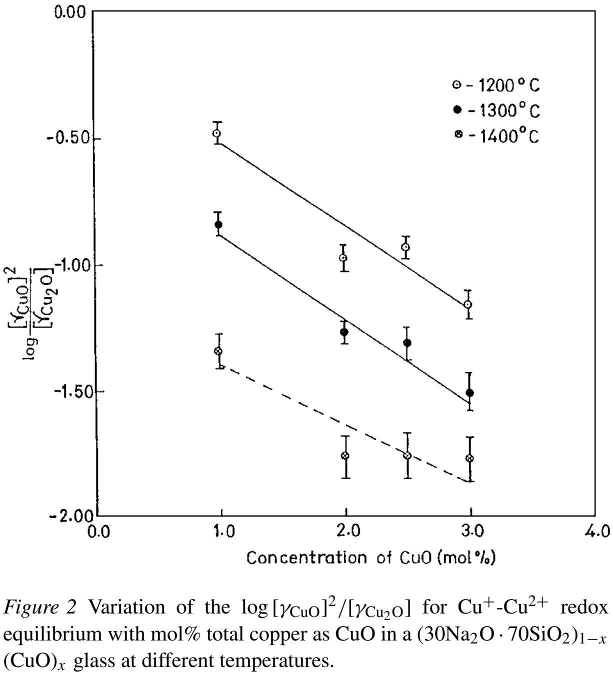

Figure 2 Variation of the log $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ for Cu^+-Cu^{2+} redox equilibrium with mol% total copper as CuO in a $(30Na_2O \cdot 70SiO_2)_{1-x}$ $(CuO)_x$ glass at different temperatures.

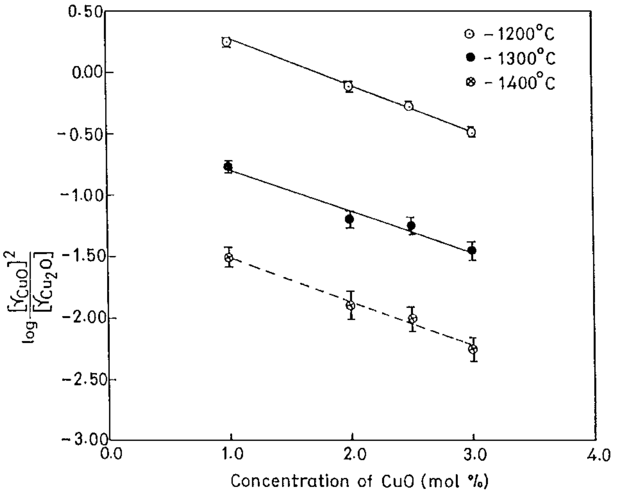

Figure 3 Variation of the $\log [\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ for Cu^+-Cu^{2+} redox equilibrium with mol% total copper as CuO in a $(30K_2O \cdot 70SiO_2)_{1-x}$ $(CuO)_x$ glass at different temperatures.

equilibrium in glasses is more vital. The results observed with Cu^+/Cu^{2+} redox pairs are analogous to the general behaviour of other redox systems in glasses.

Since, $\log [\gamma_{CuO}]^2/[\gamma_{Cu_2O}] < 1$, the logarithmic ratios of the activity coefficients of CuO to Cu_2O in alkali silicate melts at high temperatures were found to exhibit negative deviations from Raoultian ideal behaviour which may be attributed due to different structural arrangements of Cu^{2+} and Cu^+ ions in glasses where Henry's law is not obeyed including lithium silicate glass too.

When a glass containing smaller quantities of multivalent elements is melted without its significant compositional change then it is a fact that the proportions of the equilibrium concentrations of oxidised to reduced species of the element would be independent of its initial total redox introduced in the glass. In the present alkali copper silicate glasses the additions of copper oxide in the range of 1.0–3.0 mol% CuO may affect the glass compositions considerably resulting in a change of R_2O/SiO_2 ratios ($R^+ = Li^+$, Na^+ and K^+ ions) in the same proportions. It has been discussed previously as mentioned here that a decrease in the concentration of SiO_2 on adding CuO would not cause any effect on Cu^{2+}/Cu^+ ratio at equilibrium but a change in concentrations of alkali oxides in the same order would significantly affect the same which is evident from earlier studies [21–24] on O^{2-} ion activity and its influence on redox equilibrium in silicate glasses. In binary alkali silicate glasses it has been also shown by Pyare and Nath [21] that the relative oxygen ion activity increases with increasing concentrations of alkali oxides. The solubilities of gases in glasses as pointed out by earlier workers [25–27] depend not only on partial pressure of the gas above the molten glass but also on the oxygen ion activity inside the melt. Keeping this in view, Singh *et al.* [10] assumed that the solubility of O_2 in the glass melt must also depend upon its O^{2-} ion activity. The additions of mol% CuO in the present alkali silicate glasses considerably influence the glass compositions affecting its Li_2O, Na_2O and K_2O contents.

The O^{2-} ion formed due to dissociation of two nonbridging oxygen's according to following reaction

$$2(-O^-) \rightleftharpoons (-O-) + (O^{2-}) \tag{9}$$

increases its oxygen ion activity with increasing basicity of the glass as well as increasing ionic radii of alkali ions in the glass which must have continuously increased the logarithmic ratio of activity coefficients of CuO and Cu_2O in the glass (Figs 1–3). In other words, activity coefficient of CuO, γ_{CuO}, increases simultaneously with a decrease in the value of γ_{Cu_2O} with decreasing total CuO concentration and vice-versa increasing O^{2-} ion activity of the glass. This also shows that the Cu^+-Cu^{2+} redox equilibrium shifts more towards cupric state with increasing O^{2-} ion activity of the glass as evident from Figs 1–3. The tendency of the logarithmic ratio of $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ for an approach towards unity on reducing molar concentration of total CuO is an indication towards formation of an ideal Raoultian solution of copper in the glass.

In borate, phosphate and silicate glasses, it has been reported by earlier workers [28, 3, 4, 29, 30, 5, 6, 24] that Cu^+ ion can be present in octahedral symmetry due to its complete $3d^{10}$ closed shell structure whereas the Cu^{2+} ion with $3d^9$ configuration would be present as distorted octahedral symmetry in glasses because of its one unpaired electron in d-shell. Since, Cu^{2+} ion has a shorter ionic radius and greater field strength than Cu^+ ion in the glass, therefore it is expected to make the glass structure more stable. Bae and Weinberg [29] have also reported that the attainment of Cu^+-Cu^{2+} redox equilibrium would be determined by oxygen ion activity in copper phosphate glasses containing 40–60 mol% CuO in air atmosphere as a function of temperature in quartz or alumina crucibles. They also mentioned that the structural arrangements of the ions of copper had played a vital role in establishing the Cu^+-Cu^{2+} redox equilibrium in their phosphate glasses in air atmosphere. Singh and Kumar [3] had studied the absorption characteristics of cupric ion in binary alkali silicate glasses and reported the shift of the absorption band towards higher wavelength with increasing ionic radii of alkali ions. Based on their observations it is found that the ligand field stabilisation energy in distorted octahedral co-ordination of Cu^{2+} ion is higher in lithium silicate than sodium silicate than corresponding potassium silicate glass. The previous workers [31–33] have also mentioned that the oxygen present in the alkali silicate glass matrix are more closely packed in Li_2O-SiO_2 than Na_2O-SiO_2 than K_2O-SiO_2 system. In view of this it seems to be obvious that the value of $\log [\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ must also increase with increasing O^{2-} ion activity on molar replacement of Li_2O by Na_2O and Na_2O by K_2O in, silicate glasses at a particular temperature (Table I and Figs 1–3).

On plotting $\log [\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ against reciprocal of temperature three almost parallel straight lines were obtained within an experimental error of ±5% for each series of alkali copper silicate glasses as shown in Figs 4–6. Applying the following Equation 10 for the variation of logarithm of $[\gamma_{CuO}]^2/[\gamma_{Cu_2O}]$ with

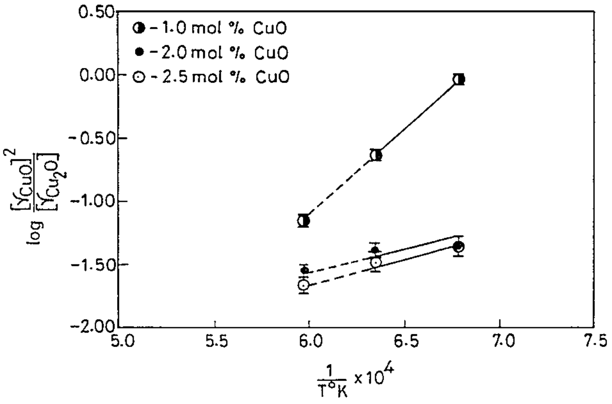

Figure 4 Variation of logarithm of activity coefficients ratio for oxides of copper with reciprocal temperature in $(30Li_2O \cdot 70\ SiO_2)_{1-x}\ (CuO)_x$ glass.

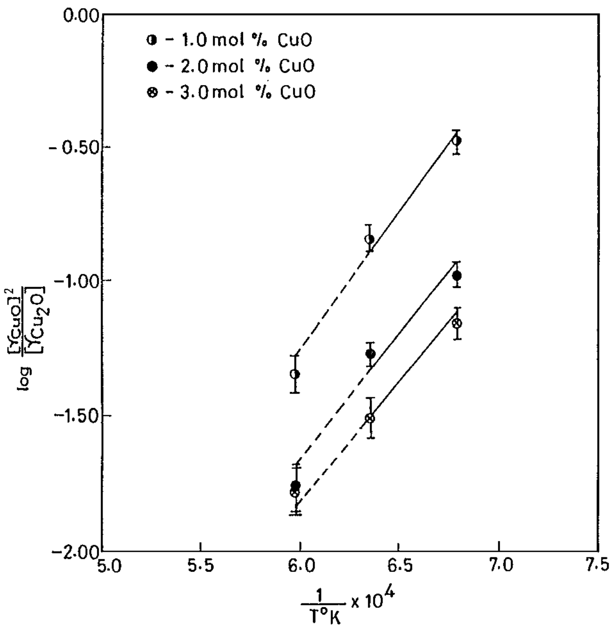

Figure 5 Variation of logarithm of activity coefficients ratio for oxides of copper with reciprocal temperature in $(30Na_2O \cdot 70SiO_2)_{1-x}\ (CuO)_x$ glass.

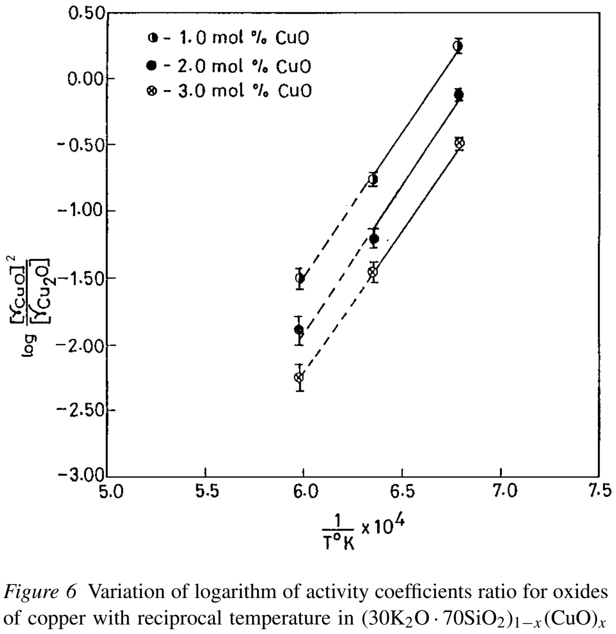

Figure 6 Variation of logarithm of activity coefficients ratio for oxides of copper with reciprocal temperature in $(30K_2O \cdot 70SiO_2)_{1-x}(CuO)_x$ glass.

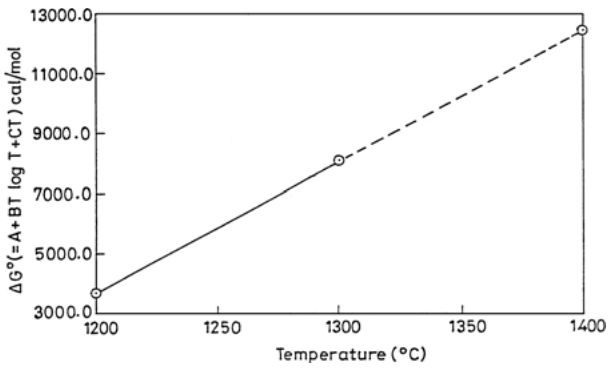

Figure 7 Ellingham diagram for the variation of change in free energy with temperature for $Cu_2O + {}^1/_2O_2 \rightleftharpoons 2CuO$ equilibrium reaction at $pO_2 = 0.21$ atmosphere.

reciprocal temperature the change in enthalpies, ΔH^M, for the partial molar mixing of Cu_2O and CuO in glasses were calculated.

$$\log\frac{[\gamma_{CuO}]^2}{[\gamma_{Cu_2O}]} = \frac{\Delta H^M}{4.576}\cdot\frac{1}{T} + C \qquad (10)$$

The average values of ΔH^M for the cuprous—cupric redox equilibrium reactions were presently found to be 4.165, 9.145 and 21.705 $k \cdot cal \cdot mol^{-1}$ in Li_2O-CuO-SiO_2, Na_2O-CuO-SiO_2 and K_2O-CuO-SiO_2 glasses, respectively. The positive values of ΔH^M for the equilibrium reaction shows that the process of partial molar mixing of Cu_2O and CuO is endothermic in glasses. Similar results were also observed previously for Ni^o-Ni^{2+} and V^{4+}-V^{5+} equilibrium reactions in silicate and borate glasses, respectively during which heat was being absorbed. However, Banerjee and Paul [11], Singh *et al.* [10] as well as Cable and Xiang [12] found the cuprous-cupric redox equilibrium reactions to be exothermic in borate and silicate glasses on applying the integrated form of van't Hoff equation in order to calculate the enthalpy change, ΔH^M per mole of the product. The Ellingham's diagram as shown in Fig. 7 was made on plotting standard free energy change, ΔG^o with temperature for oxidation-reduction equilibrium reaction (1) between oxides of copper in air. The value of ΔG^o for the reaction (1) was obtained by extrapolating the Ellingham line upto 1400°C for calculating the activity coefficients of Cu_2O and CuO in glasses. The straight line as shown in Fig. 7 with a constant slope indicates that the present reaction occurs involving homogeneous oxide phase.

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