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# Thermodynamics of $Cr^{3+}$–$Cr^{6+}$ equilibrium in borate melts

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The $Cr^{3+}$–$Cr^{6+}$ equilibrium was studied in lithium and sodium aluminoborate melts in an air atmosphere at different temperatures. A mechanism of the $Cr^{3+}$–$Cr^{6+}$ redox reaction in glass melts has been suggested. Enthalpy and entropy of the reaction in molten borates were calculated and the results thus obtained have been discussed thermodynamically.

## 1. Introduction

Irmann [1] studied $Cr^{3+}$–$Cr^{6+}$ equilibrium in molten binary borates containing the oxides of Li, K, Ba, Cd and Zn under different partial pressures of oxygen. For a constant partial pressure of oxygen, a minima was observed in each series of lithium, barium and zinc borate melts when $\log(Cr^{6+})/(Cr^{3+})$ was plotted against the mol per cent of metal oxides; however, for lead and potassium borate melts the $\log(Cr^{6+})/(Cr^{3+})$ plot increased progressively with increased additions of metal oxides. For a glass of constant composition at a fixed temperature the constant, $K'$,

$$K' = \frac{(Cr^{6+})}{(Cr^{3+})(pO_2)^{3/4}} \qquad (1)$$

was found to remain constant on varying the chromium concentration within the range 0.1 to 1.0 wt% as $Cr_2O_3$. On plotting $\log(Cr^{6+})/(Cr^{3+})$ against $\log(pO_2)$ a straight line with a slope of $\frac{3}{4}$ was obtained which indicated that Equation 1 represents the equilibrium reaction and can be represented by

$$\underset{\text{(melt)}}{Cr^{3+}} + \tfrac{3}{4}O_2 \rightleftharpoons \underset{\text{(melt)}}{Cr^{6+}}. \qquad (2)$$

Thus $K'$ was considered as an apparent equilibrium constant for the reaction represented by

$$K' = \frac{(Cr^{6+})}{(Cr^{3+})(pO_2)^{3/4}}. \qquad (3)$$

As Equation 2 is unbalanced, Nath and Douglas [2, 3] modified it to

$$Cr^{3+} + \tfrac{3}{4}O_2 \rightleftharpoons Cr^{6+} + \tfrac{3}{2}O^{2-} \qquad (4)$$

and discussed their results. On plotting $\log(Cr^{6+})/(Cr^{3+})(pO_2)^{3/4}$ against mol% alkali oxides for binary alkali silicate glasses, three separate straight lines were obtained, for the lithium, sodium and potassium silicate series of glasses, the slopes of which were inversely proportional to the field strength of alkali ions. To study the effect of temperature Nath and Douglas heat treated 4, 5 and 10 g samples of the glass in alumina crucibles for different lengths of time at 950, 1100 and 1400° C, respectively. During this study the depth and surface area of each glass exposed to the furnace atmosphere was not constant and hence the rate of approach to equilibrium at various temperatures cannot be compared.

Nath and his co-workers [4–6] observed minima in each series of binary borate melts containing the oxides of Li, Na, K, Ca, Sr, Ba, Pb, Cd and Zn. It was further found that the $Cr^{3+}$–$Cr^{6+}$ redox equilibrium shifted more towards the reduced state with increasing bond strength between non-bridging oxygen ions and modifying cations [6, 7]. Singh [8] calculated the rate constants for the $Cr^{3+}$–$Cr^{6+}$ equilibrium in sodium aluminoborate glass for different concentrations of redox ions at 1000° C. The rate constant decreased with increasing concentration of redox ions. Since the equilibrium was studied at

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only one temperature, thermodynamic data could not be calculated. The literature survey shows that very little work has been performed to study the thermodynamics of the $Cr^{3+}$–$Cr^{6+}$ redox reaction in glass and, hence, in the present investigation these studies were undertaken.

## 2. Experimental procedure

Ternary aluminoborate glasses having the compositions 15 mol% $Li_2O \cdot 10$ mol% $Al_2O_3 \cdot 75$ mol% $B_2O_3$ and 15 mol% $Na_2O \cdot 10$ mol% $Al_2O_3 \cdot 75$ mol % $B_2O_3$ were selected as base glasses since it is easy to dissolve them in dilute sulphuric acid without disturbing the $Cr^{3+}$–$Cr^{6+}$ equilibrium [4, 6, 9]. The results on the determination of trivalent and hexavalent chromium in glasses obtained by chemical methods have been earlier compared with those obtained by spectrophotometric methods and results from the two approaches have been found to agree well [9, 10]. The chemicals used for preparing the glass batches were of analytical reagent grade, except for the aluminium hydroxide which was of laboratory reagent grade. 0.04 to 0.06 wt% Cr was introduced in the form of ammonium dichromate.

Glasses were melted in a 100 ml platinum–2 wt % rhodium crucible kept in an electric furnace at about 1150° C for four hours. To ensure homogeneity, after four hours of melting, glasses were poured onto an aluminium sheet, crushed and remelted for another two hours. 10 gm specimens of these glasses were heat-treated at a constant temperature in air for different lengths of time in 25 ml platinum crucibles. Nath and Douglas [3] have reported that platinum does not interfere with $Cr^{3+}$–$Cr^{6+}$ equilibrium. The temperature was controlled within ± 5° C by an automatic temperature controller. After heat-treatment, the melts were air-quenched and chemically analysed for hexavalent and total chromium contents by the diphenylcarbazide method [4, 6]. When the proportion of chromium present in the hexavalent state did not change with time within the experimental error of ± 5% at a particular temperature it was concluded that equilibrium was established (see Fig. 1).

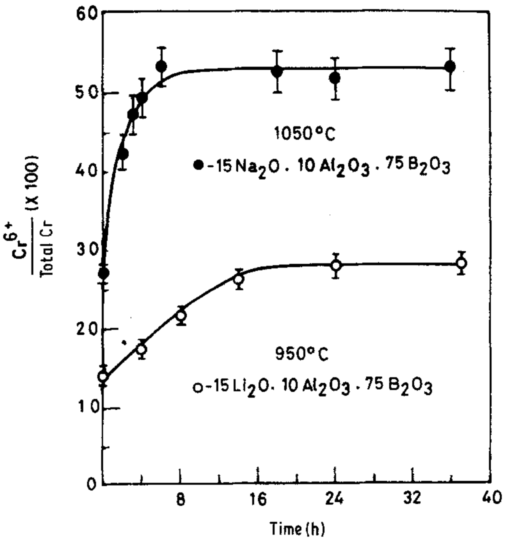
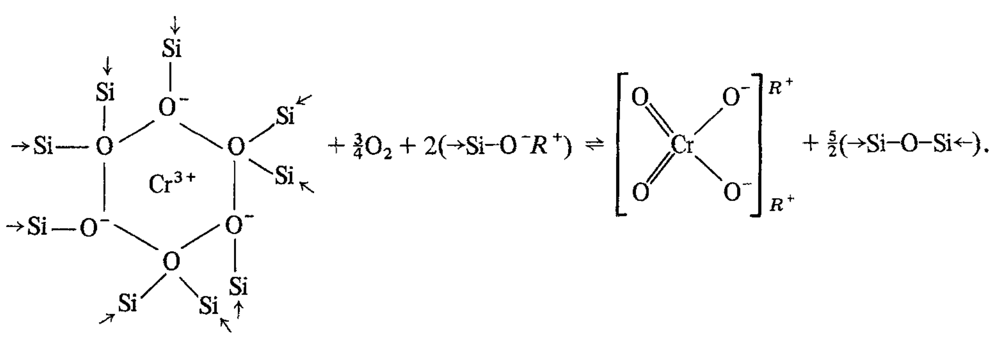


*Figure 1* Relation between the proportion of hexavalent chromium and the duration of heat-treatment.

## 3. Results and discussion

The results summarized in Tables I and II and Fig. 2 show that the $Cr^{3+}$–$Cr^{6+}$ equilibrium shifts more towards the reduced state with increasing temperature.

Nath and Tyagi [11] critically examined the equations used by various workers [1–3, 12–14] to represent the $Cr^{3+}$–$Cr^{6+}$ equilibrium reaction and finally suggested the following equation, assuming that the three (→ Si–O–Si ←) groups attached to the $Cr^{3+}$ complex do not take part in the reaction, where $R$ represents alkali ions, such that:



(5)

TABLE I The effect of temperature on the $Cr^{3+}$–$Cr^{6+}$ equilibrium in lithium aluminoborate melt

| Temperature (° C) | Duration of heat-treatment (h) | Concentration of chromium as Cr | | log $K'$ | $\Delta S$ (cal $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|
| | | Hexavelent chromium (wt %) | Total chromium (wt %) | | |
| 950 | 0 | 0.0047 | 0.0349 | | |
| 950 | 4 | 0.0058 | 0.0342 | | |
| 950 | 8 | 0.0064 | 0.0302 | | |
| 950 | 14 | 0.0071 | 0.0274 | | |
| 950 | 24 | 0.0068 | 0.0250 | | |
| 950 | 37 | 0.0065 | 0.0233 | 0.092 | −9.3 |
| 1025 | 12 | 0.0082 | 0.0346 | | |
| 1025 | 24 | 0.0074 | 0.0325 | −0.010 | −8.8 |
| 1100 | 4 | 0.0079 | 0.0373 | | |
| 1100 | 8 | 0.0075 | 0.0373 | −0.074 | −8.3 |

Although this equation can explain the observed results it does not indicate the mechanism of electron transfer in glasses. Recently it has been pointed out [15, 16] that electron transfer in glasses probably takes place in stages, as is known to be the case in aqueous solutions.

It is known that most electropositive elements form simple ionic peroxides containing $O_2^{2-}$ ions [17]. Similarly, in glass melts containing electropositive elements such as Li, Na and K, the oxygen molecule probably reacts with the $O^{2-}$ ion present in the melt to form a peroxide ion which oxidises the redox ion from a lower valency state to a higher valency state. This process can be represented by

$$\tfrac{3}{2}O^{2-} + \tfrac{3}{4}O_2 \rightleftharpoons \tfrac{3}{2}O_2^{2-}; \tag{6}$$

$$[(\text{–O–})_3Cr^{3+}(\text{–O}^-)_3] + \tfrac{3}{2}O_2^{2-} \rightleftharpoons (CrO_4)^{2-} + 4(\text{–O–}) + (\text{–O}^-); \tag{7}$$

$$3(\text{–O}^-) \rightleftharpoons \tfrac{3}{2}O^{2-} + \tfrac{3}{2}(\text{–O–}). \tag{8}$$

Combining Equations 6, 7 and 8 gives

$$\underset{\substack{\text{chromic complex}\\ \text{in melt}}}{[(\text{–O–})_3Cr^{3+}(\text{–O}^-)_3]} + \underset{\text{gas}}{\tfrac{3}{4}O_2} + \underset{\text{melt}}{2(\text{–O}^-)}$$

TABLE II The effect of temperature on the $Cr^{3+}$–$Cr^{6+}$ equilibrium in sodium aluminoborate melt

| Temperature (° C) | Duration of heat-treatment (h) | Concentration of chromium as Cr | | log $K'$ | $\Delta S$ (cal $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|
| | | Hexavalent chromium (wt %) | Total chromium (wt %) | | |
| 950 | 24 | 0.0216 | 0.0373 | | |
| 950 | 36 | 0.0205 | 0.0359 | | |
| 950 | 40 | 0.0203 | 0.0356 | 0.636 | −11.1 |
| 1000* | 33 | 0.0424 | 0.0762 | | |
| 1000* | 40 | 0.0422 | 0.0760 | | |
| 1000* | 50 | 0.0420 | 0.0758 | | |
| 1000* | 60 | 0.0418 | 0.0755 | 0.604 | −10.7 |
| 1050 | 0 | 0.0109 | 0.0410 | | |
| 1050 | 2 | 0.0164 | 0.0390 | | |
| 1050 | 3 | 0.0174 | 0.0370 | | |
| 1050 | 4 | 0.0174 | 0.0363 | | |
| 1050 | 6 | 0.0181 | 0.0342 | | |
| 1050 | 18 | 0.0171 | 0.0328 | | |
| 1050 | 24 | 0.0154 | 0.0301 | | |
| 1050 | 36 | 0.0144 | 0.0274 | 0.547 | −10.3 |
| 1100 | 10 | 0.0229 | 0.0537 | | |
| 1100 | 15 | 0.0227 | 0.0530 | | |
| 1100 | 20 | 0.0210 | 0.0503 | 0.365 | −9.9 |

*Data has been taken from [8].

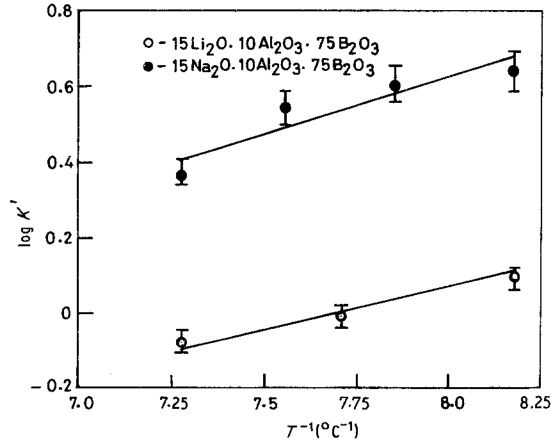


*Figure 2* Variation of log $K'$ with reciprocal temperature.

$$\rightleftharpoons \underset{\substack{\text{chromate}\\ \text{complex}\\ \text{in melt}}}{(\mathrm{CrO_4})^{2-}} + \underset{\text{melt}}{\tfrac{11}{2}(\text{–O–})} \qquad (9)$$

$$\frac{(\text{chromate complex})}{(\text{chromic complex})(\mathrm{pO_2})^{3/4}} = K'$$

$$= K\frac{(\text{–O}^-)^2}{(\text{–O–})^{11/2}}\,. \qquad (10)$$

Since the concentrations of redox ions in glasses are sufficiently low for the application of Equation 9, their activities have been replaced by their concentrations. A similar assumption has also been made by Nath and Douglas [3] for even higher concentrations of redox species present in glasses. The concentrations of non-bridging and bridging oxygen in a glass at a particular temperature are very high. Taking into consideration the activity coefficients of ($-$O$^-$) and (–O–) oxygens, Equation 10 can be written as

$$\frac{(\text{chromate complex})}{(\text{chromic complex})(\mathrm{pO_2})^{3/4}} = K'$$

$$= K\frac{\beta^2(\text{–O}^-)^2}{\alpha^{11/2}(\text{–O–})^{11/2}}\,, \qquad (11)$$

where $\beta$ and $\alpha$ are the activity coefficients of ($-$O$^-$) and (–O–) oxygens, respectively.

The observed results can be explained on the basis of the above equations. The concentrations of bridging and non-bridging oxygens in a glass are very high in comparison with the concentration of O$^{2-}$ ions at a particular temperature. On changing the temperature, the O$^{2-}$ ion concentration varies but the concentrations of ($-$O$^-$) and (–O–) oxygens remain nearly constant.

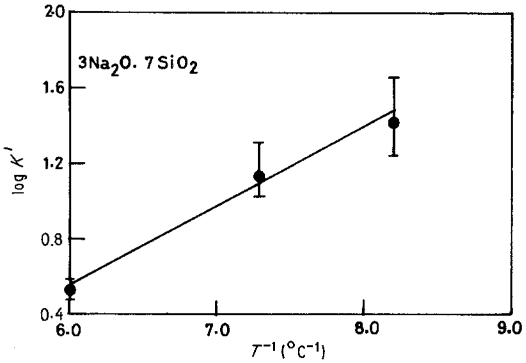


*Figure 3* Variation of log $K'$ with reciprocal temperature.

Applying the integrated form of the van 't Hoff equation to Equation 11 yields:

$$\log K' = -\frac{\Delta H}{4.576}\frac{1}{T} + \text{constant}, \qquad (12)$$

where $\Delta H$ is the enthalpy. In Fig. 2 $\log K'$ was plotted against $T^{-1}$(K) and two nearly parallel straight lines were obtained. From their slopes the values of the enthalpy, $\Delta H$, were calculated and found to be $-11.4$ and $-13.6$ kcal mol$^{-1}$ in lithium and sodium aluminoborate melts, respectively. The negative value of $\Delta H$ indicates that the reaction in Equation 9 is exothermic which explains why the reaction proceeds more towards the reduced state with increasing temperature. Closer values of $\Delta H$ for lithium and sodium aluminoborate melts also indicate that similar reactions are taking place in these glass melts. Using the data given by Nath and Douglas [2, 3], the enthalpy for the Cr$^{3+}$–Cr$^{6+}$ reaction in silicate glass was calculated by the present authors from the slope of the straight line shown in Fig. 3 and was found to be $-19.0$ kcal mol$^{-1}$. The difference in the values of $\Delta H$ obtained is probably due to the considerable differences in base glass composition.

The free energy change, $\Delta G$, for a chemical reaction is given by

$$\Delta G = \Delta H - T\Delta S, \qquad (13)$$

where $\Delta S$ is the change in entropy. At equilibrium,

$$(\Delta G)_{T,P} = 0, \qquad (14)$$

where $P$ is pressure. Hence, Equation 13 yields

$$\Delta S = \frac{\Delta H}{T}\,. \qquad (15)$$

The entropy changes, $\Delta S$, for the $Cr^{3+}$–$Cr^{6+}$ reaction, Equation 9, were calculated from Equation 15 and are presented in Tables I and II. The values of $\Delta S$ for both the series of glasses increase with increasing temperature which indicate increasing disorder in the glass melts.

## Acknowledgements

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