

TABLE 2. STABILITY CONSTANTS OF COBALT(II) BROMIDE COMPLEXES
VALID FOR 20° AND 0.691 M PERCHLORIC ACID

$\beta_1 = 0.74 \pm 0.1 \text{ M}^{-1}$	$\beta_2 = 0.38 \pm 0.1 \text{ M}^{-2}$
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introduced by Fronaeus,¹ with the resin, Amberlite IR-120 (30–80 mesh), in the hydrogen form. The experimental procedure, which involved the use of ⁶⁰Co as a tracer, was generally similar to that described in a previous communication.²

The distribution ratios measured at 20°C and the functions necessary for the derivation of stability constants are given in Table 1. The notation and method of calculation have been described by Morris and Short.² The results obtained for the stability constants, $\beta_j = [\text{CoBr}^{(2-j)+}]/[\text{Co}^{2+}][\text{Br}^-]^j$, are presented in Table 2. Our study provides no evidence for the existence of complexes with $j > 2$ in solution in the range $[\text{Br}^-] \leq 0.58 \text{ M}$, though anionic species are known to be formed at higher bromide concentrations.³

In the case of cobalt(II) it appears that chloride complexes are stronger than corresponding bromide complexes.

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ON THE ELECTROCHEMICAL BEHAVIOUR OF MOLTEN NITRITES*

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THE results obtained for the electrolysis of molten nitrates^{1–3} encouraged us to investigate the electrochemical behaviour of molten nitrites, as the processes involved might be related to those previously described for the molten nitrates. This preliminary report deals with the results obtained during electrolysis of pure molten sodium nitrite at *ca* 290°C.

Molten salt was electrolysed in a Pyrex glass container provided with a platinum anode, its potential being measured against a silver/silver-ion (Ag^+ , 2×10^{-3} mole fraction) reference electrode in the eutectic $\text{KNO}_3\text{--NaNO}_3$ (1:1), placed in a special container with a Luggin–Haber capillary tip.

The electrolysis was performed with the electrodes placed in different compartments to separate the products yielded by the cathodic and anodic reactions and to maintain a constant gas composition of the gaseous mixture in the anodic section of the cell. The current/voltage curves were measured in the usual way. The anodic current density was varied between 1.5×10^{-5} to $2.4 \times 10^{-1} \text{ A/cm}^2$.

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The anodic reaction is represented by



NO_2 was identified as the product yielded by the anodic reaction.

When the electrolysis current was switched off, a reversible cell was formed between the working electrodes of the cell. The potential of the anode measured against the reference electrode was -0.300 V at 306°C . This formation of a reversible electrode at the platinum anode has also been demonstrated by measuring its potential against a sodium/sodium-ion reversible electrode in pure molten sodium nitrate. The emf of the $\text{Na}/\text{NaNO}_2/\text{NO}_2$, Pt cell is 2.72 V at 306°C . The potential of the residual cell formed after the interruption of the electrolysis current was independent of the current intensity that previously flowed through the cell and showed typical reversible behaviour. Considering the reported value for the standard reversible potential of nitrate electrode referred to the standard sodium electrode,² the difference between the standard reversible potential of nitrate and nitrite NO_2 electrodes at 306°C is 0.825 V.

The current/voltage curves indicate the existence of an overpotential. The Tafel slope is 109 ± 5 mV at 277°C . This value is quite close to $2.303 RT/F$, and it indicates that the transfer coefficient α is unity. The Tafel slope was also determined by measuring the rate of decay of the anodic overpotential at current interruption. The overpotential decayed logarithmically with time and the average slope obtained from overpotential *vs* $\log t$ plots was 109 ± 5 mV, in good agreement with the figure resulting from current/voltage curves as mentioned above.

A detailed discussion of the foregoing effects will be published shortly.

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