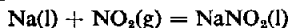


A NITRITE REVERSIBLE ELECTRODE*

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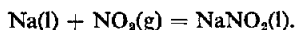
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Abstract—A galvanic cell involving the formation of sodium nitrite according to



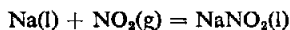
is described. The existence of a reversible nitrite electrode is reported and the dependence of its potential on nitrite ion concentration, nitrogen dioxide pressure and temperature is shown.

Résumé—On décrit une cellule galvanique qui implique la formation de nitrite de sodium moyennant la réaction



On signale l'existence d'une électrode de nitrite réversible et on démontre que son potentiel dépend de la concentration des ions nitrite, de la pression du dioxyde de nitrogène et de la température.

Zusammenfassung—Eine galvanische Zelle, in welcher die Bildung von Natriumnitrit mittels der Reaktion



abläuft wird beschrieben. Es wird über das Bestehen einer reversiblen Nitritelektrode berichtet und ihre Abhängigkeit von der Nitritionenkonzentration und dem Stickstoffdioxidpartialdruck sowie der Temperatur wird gezeigt.

INTRODUCTION

DURING a study of the electrochemical behaviour of molten nitrite,¹ the formation of a residual cell after the interruption of the electrolysis current was observed. The response of the cell resembled the behaviour of a reversible galvanic cell formed during the electrolysis of the molten nitrate already described.^{2,3} As in that case, the residual cell disappeared when nitrogen dioxide was swept out from the anodic section. The experimental conditions for the formation of the reversible nitrite electrode thus suggest that it was built up during the electrolysis of the molten nitrite on platinum electrodes, yielding a reproducible and stable rest potential after current interruption.

As a further support of the existence of the reversible nitrite electrode, the study of a chemical type galvanic cell involving the formation reaction of molten sodium nitrite from molten sodium and gaseous nitrogen dioxide has been attempted in the present work. This aim could be achieved because the reversibility of the sodium/sodium-ion electrode in the molten state has already been well established⁴ and, consequently, it is possible to obtain reliable quantitative information about the nitrite electrode in the molten state.

EXPERIMENTAL

Two different types of electrolysis cells were used. Both were made of Pyrex glass. The first was designed to study the nitrite electrode either against a sodium/sodium-ion or a silver/silver-ion reference electrode, the latter dissolved in the sodium-nitrate-potassium-nitrate eutectic and involving a liquid junction. These

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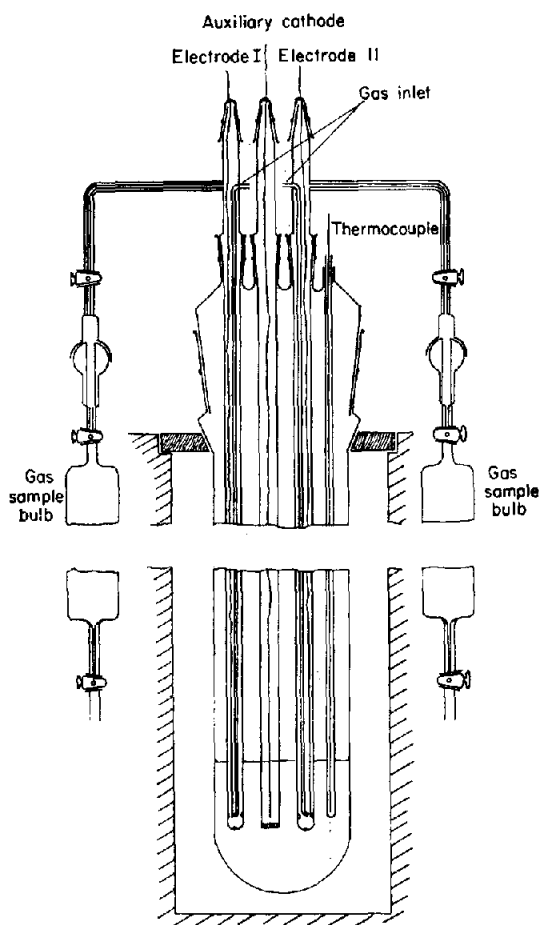


FIG. 1. Diagram of the NO_2 concentration cell.

cells were similar to the one described in a previous publication.² A second cell, shown in Fig. 1, was employed to determine the effect of nitrogen dioxide pressure on the electrode potential. It consisted of a set of two symmetrical electrodes having platinum contacts and properly placed inlets and outlets for flowing gas mixtures of different composition. The cell sections were connected to gas sample bulbs, in which the equilibrium mixtures could be obtained for analysis.

Various electrolytes were used (i) pure sodium nitrite (ii) solutions of sodium nitrite in sodium-nitrate-potassium-nitrate eutectic. A critical experimental detail for attaining the formation of the cell was the elimination of traces of water. After a previous drying in an oven at about 150°C , the electrolytes were dried in the cell by evacuation at a temperature above their melting point for a period of about 5 h.

Experiments were performed in the temperature range from 280 to 330°C . The cell was kept in an air thermostat within 0.2°C . The rest potential was read with a Houston DC Potentiometric Voltmeter HB-160, with $10\text{ M}\Omega$ impedance input and 0.3 per cent accuracy.

RESULTS AND INTERPRETATION

1. Results with the pure sodium nitrite

The formation of the cell was achieved by electrolysing the molten salt at a constant current density ranging from 50 to 200 mA/cm², long enough to allow the accumulation of an appreciable amount of electrolysis products. The total reaction occurring in the cell during electrolysis is



After the interruption of the current a molten sodium electrode was formed in the cathode of the electrolysis cell while the other electrode comprised an electrochemical system formed by molten sodium nitrite saturated with nitrogen dioxide at nearly atmospheric pressure. The cell was designed to avoid any alteration of the system once the rest potential was established.

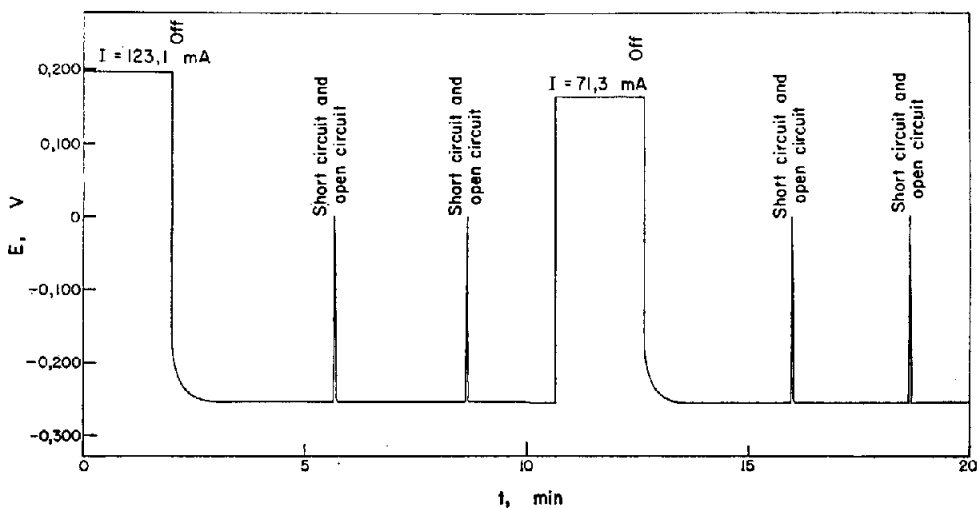


FIG. 2. Formation and test of the nitrite electrode. Reference electrode: Ag/AgNO₃ ($x = 3.2 \times 10^{-3}$)-NaNO₂-KNO₃. 289.6°C. Electrolysis current as indicated.

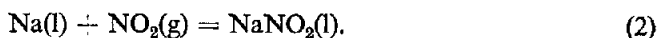
The residual potential, measured approximately 1 min after interrupting electrolysis, attained a steady value. This is shown in Fig. 2 for experiments in which the potential of the nitrite electrode was measured against a reversible silver/silver-ion reference electrode. Values of the emf of the residual cell formed after electrolysing pure sodium nitrite are assembled in Table 1. Values of the residual potential corresponding to the cell formed with the anode and the silver/silver-ion reference electrode are assembled in Table 2. In either case the emf of the residual cells was independent of the electrical current applied to electrolyse the melt. It was also observed that the final steady potential kept constant, within a few millivolts, for at least one hour of the electrolysis interruption, if no alteration of the system occurred.

The potential difference behaved as the emf of a reversible cell when it was tested in the way previously described.^{2,3} Therefore, the emf of the residual cell, in absolute terms, should be considered as the reversible decomposition potential of molten

TABLE 1. CELL: Na(l)/NaNO₂(l)/NO₂(g,
p = 1), Pt

Temp. °C	<i>E</i> _{exp} V
280.0	2.776 ± 0.015
287.0	2.775 ± 0.025
295.3	2.755 ± 0.015
306.0	2.720 ± 0.025
307.0	2.720 ± 0.015
307.0	2.730 ± 0.015
312.0	2.690 ± 0.025
316.5	2.691 ± 0.015
319.0	2.699 ± 0.015
330.0	2.665 ± 0.015

sodium nitrite, assuming the total reaction involved in the cell is the formation of sodium nitrite according to



At the experimental temperatures nitrogen dioxide is partially dissociated into nitric oxide and oxygen.⁵

2. Effect of nitrite-ion concentration and nitrogen-dioxide partial pressure

If (2) represents the cell reaction, the partial equilibrium involved in the nitrite electrode is



and its potential given by

$$E = E^\circ + \frac{RT}{zF} \ln \frac{[\text{NO}_2]}{[\text{NO}_2^-]}. \quad (4)$$

To test (4), the concentration of nitrite ion was changed by using different nitrite solutions in molten sodium-nitrate-potassium-nitrate. In these cases the cell was formed by electrolysing the mixture at a potential sufficiently low to avoid nitrate decomposition. The procedure was based on the knowledge of the current/voltage curves for the different mixtures.⁶ Results are assembled in Table 3. There, average values of the emf, *E*_{exp}, and the sodium-nitrate mole fraction, *x*, are indicated, as well as the expected value of the emf, *E*_{cal}, from (4), assuming unit activity coefficients. At lower concentrations the agreement is satisfactory; at higher ones a deviation occurs, showing that the mean activity coefficients of sodium nitrite are appreciably less than unity, as is to be expected.

TABLE 2. CELL: Ag(s)/AgNO₃(*x*), NaNO₃-
KNO₃(l)/NaNO₂(l)/NO₂(g, *p* = 1), Pt.
x = 3.2 × 10⁻³

Temp. °C	<i>E</i> _{exp} V
289.6	-0.254
267.8	-0.240
261.8	-0.237
254.8	-0.226
232.9	-0.213

In order to observe the effect of nitrogen-dioxide partial pressure, experiments were performed by forming two nitrite electrodes and then changing the partial pressure of the nitrogen dioxide in one of them by flowing a known amount of purified nitrogen through it. When the partial pressure of the gas in one electrode was decreased the electrode potential became more negative, and for a ratio of partial

TABLE 3. CELL: Na(l)/NaNO₃(l)//NaNO₂(l)(x), NaNO₃-KNO₃(l)/NO₂(g, p = 1), Pt

Temp. °C	x mole fraction	E _{exp} V	E _{cal} V
317.0	0.00414	2.950 ± 0.025	2.976
317.0	0.0397	2.855	2.861
317.0	0.467	2.780	2.736
E _r ^o = 2.697 V			

pressures of 0.1 the emf of the gas concentration cell was 0.100–0.120 V at 300°C. Obviously the error involved in these determinations was greater than that in previous experiments, but the effect is in agreement with (4).

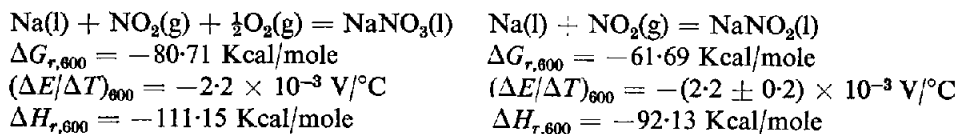
3. Thermodynamic data from the chemical cell

Unfortunately there are not enough thermal data available to evaluate with accuracy the emf of the chemical galvanic cell represented by (2). However, a comparison between the emf of the sodium nitrite and sodium nitrate formation cells, involving the equilibria already known, is useful as regards the thermochemical data of the corresponding reactions.

From the standard emf, the change of free energy at temperature *T* is known, and according to

$$\Delta G_{r,T}^{\circ} = \Delta H_{r,T}^{\circ} - T\Delta S_{r,T}^{\circ}, \quad (5)$$

the enthalpy change, $\Delta H_{r,T}$, can be obtained because the entropy change, $\Delta S_{r,T}$, can be evaluated from the temperature coefficient of the cells. Thus, for sodium nitrate and sodium nitrite respectively, at 600°K, we have:



The difference in the enthalpy changes is close to the difference of the enthalpies of formation of sodium nitrate and sodium nitrite at 298.16°K.⁷

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