# A REVERSIBLE CHEMICAL CELL OF MOLTEN POTASSIUM NITRATE*

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Abstract—A reversible galvanic cell of molten potassium nitrate is described. It is represented by the following scheme:

$$K(l)/KNO_3(l)/NO_2(g),O_2(g)/Pt(s).$$

The theoretical standard emf calculated from thermochemical data for the reaction

$$K(l) + NO_2(g) + \tfrac{1}{2}O_2(g) = KNO_3(l)$$
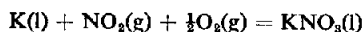
is in very good agreement with the one deduced from the experimental results. The standard emf of the cell is given by

$$E^\circ = 5 \cdot 440 + 3 \cdot 812 \times 10^{-4}T \ln T - 6 \cdot 231 \times 10^{-8}T^2 + 2 \cdot 623/T - 5 \cdot 156 \times 10^{-3}T.$$

Résumé—On décrit une cellule galvanique réversible de nitrate de potassium fondu. Elle se représente par le schéma suivant:

$$K(l)/KNO_3(l)/NO_2(g),O_2(g)/Pt(s).$$

La fem théorique normale dérivée des données thermochimiques pour la réaction

$$K(l) + NO_2(g) + \tfrac{1}{2}O_2(g) = KNO_3(l)$$
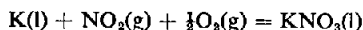
est en concordance avec celle obtenue par voie expérimentale. La fem normale de la cellule s'exprime par

$$E^\circ = 5 \cdot 440 + 3 \cdot 812 \,.\, 10^{-4}T \ln T - 6 \cdot 231 \,.\, 10^{-8}T^2 + 2 \cdot 623/T - 5 \cdot 156 \,.\, 10^{-3}T.$$

Zusammenfassung—Eine reversible galvanische Zelle mit geschmolzenem Kaliumnitrat wird beschrieben. Sie wird durch folgendes Schema dargestellt:

$$K(l)/KNO_3(l)/NO_2(g),O_2(g)/Pt(s).$$

Die theoretische Standard EMK, welche aus thermochemischen Daten für die Reaktion

$$K(l) + NO_2(g) + \tfrac{1}{2}O_2(g) = KNO_3(l)$$
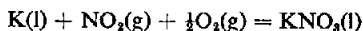
abgeleitet wurde, stimmt sehr gut mit der aus den experimentellen Ergebnissen erhalten überein. Die Standard EMK der Zelle wird durch die Gleichung

$$E^\circ = 5 \cdot 440 + 3 \cdot 812 \,.\, 10^{-4}T \ln T - 6 \cdot 231 \,.\, 10^{-8}T^2 + 2 \cdot 623/T - 5 \cdot 156 \,.\, 10^{-3}T$$

ausgedrückt.

INTRODUCTION

During a study of the electrochemical behaviour of molten nitrates, reversible chemical cells of silver, sodium and lithium nitrates were obtained[1-3] using a metal electrode and a nitrate electrode. For the sodium and lithium nitrate cells, the standard electromotive forces are, respectively, 3·401 V and 3·520 V at 371°C. These values agree quite well with those derived from thermochemical data.

Later, as part of a research on chemical cells in fused salts, many attempts were made to obtain a molten potassium nitrate chemical cell. This was of particular

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interest as it would allow a check of the emf obtained from thermochemical data already available in the literature for the whole range of temperature where the nitrate electrode proved reliable. In the course of the experimental work serious difficulties arose owing to traces of water in the molten electrolyte. This produced a lack of stability and reproducibility of the potentials obtained for the system. These difficulties were eventually overcome by means of an improved cell design and a very careful drastic dehydration process of the melt.
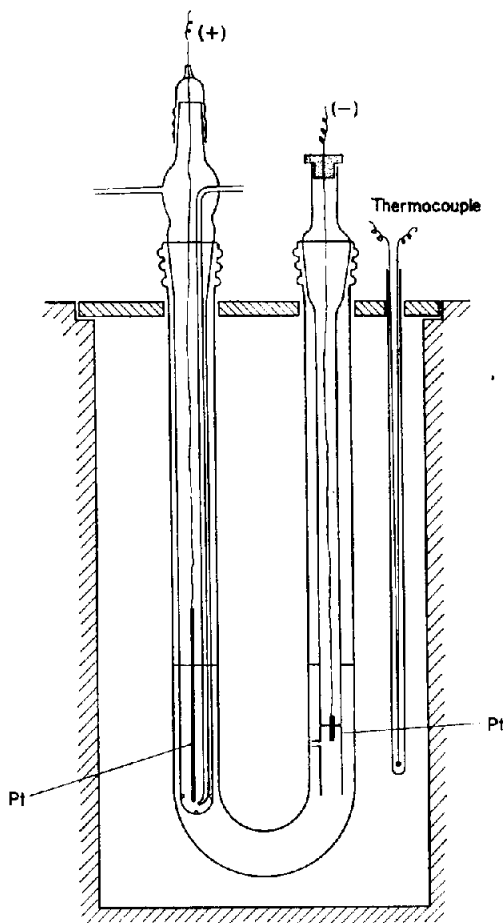

FIG. 1. Scheme of the cell.

EXPERIMENTAL TECHNIQUE

The galvanic cell was formed by electrolysis of molten potassium nitrate. For this purpose a U-type cell made of Pyrex glass Fig. 1, was employed. It contained two platinum wire electrodes which were used as anode and cathode respectively during the electrolysis of the melt. The anode was mounted as a usual gas-type electrode, having a glass compartment to maintain a constant gas composition in equilibrium with the molten salt. The cathode was constructed similar to the previously described for a sodium/sodium-ion reversible electrode[2]; this gave an alkali-metal electrode of good reproducibility.

Potassium nitrate analytical reagent from Mallinckrodt was used. First it was dried in an oven. Then it was further dehydrated in a vacuum system with the salt in the molten state and finally, it was poured into the container. These successive operations were necessary to make sure that the reversible potassium electrode would be formed.

Afterwards the salt was electrolysed for several h at current densities ranging from 100 to 500 mA/cm² referred to the apparent cathode area.

When electrolysis was interrupted the potential of the residual cell was read with a Houston DC Potentiometric Voltmeter, Model HB-160, with a 10-MΩ impedance input and 0·3 per cent accuracy.

In view of the behaviour of the nitrate electrode and the melting and decomposition temperatures of potassium nitrate,[4] the experiments were performed at temperatures from 340 to 380°C. The temperature was kept constant within 0·5°C with a conventional air thermostat.

RESULTS AND INTERPRETATION

When an incompletely dehydrated fused potassium nitrate was used, no reproducible results were obtained, mainly due to non-formation of a potassium/ potassium-ion electrode in the system. The latter, once it was formed, could be used for various days with the salt maintained in the molten state, but afterwards it broke down because the diffusion of the metal into the glass changed its composition and mechanical properties.

The total reaction occurring during the electrolysis of the salt is represented by

$$KNO_3 = K + NO_2 + \tfrac{1}{2}O_2. \tag{1}$$

The accumulation of reaction products initiates the chemical cell

$$K(l)/KNO_3(l)/NO_2(g), p = \tfrac{2}{3};\ O_2(g), p = \tfrac{1}{3}/Pt(s) \tag{I}$$
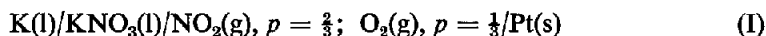
comprising a potassium and a nitrate reversible electrode. Cell I representing a galvanic cell without liquid junction is responsible for the residual emf read at current interruption. The emf attained a steady value approximately 1 min after current was switched off and it stayed constant for several h. Its value was independent of the current density for creating the cell, and its reproducibility was within 10 mV.

TABLE 1. EXPERIMENTAL EMF

Temp °C	E V
344 ± 0·5	3·69 ± 0·01
	3·70
354	3·68
	3·68
355	3·67
365	3·65
	3·64
375	3·64
380	3·62

The reversibility of the chemical cells tested in the way already indicated in previous publications also proved quite satisfactory. Values of the emf, E, at different temperatures are reported in Table 1.

The experimental emfs are related to the formation of potassium nitrate according to

$$K(l) + NO_2(g) + \tfrac{1}{2}O_2(g) = KNO_3(l). \tag{2}$$

Therefore, a theoretical study of cell I in the standard state can be done in the whole temperature range investigated, because the heat capacity at constant pressure and the

TABLE 2. THERMODYNAMIC DATA

$$C_p(KNO_3, \alpha) = 14\cdot55 + 28\cdot40 \times 10^{-3}\,T \quad (298\text{–}401°K)$$
$$\Delta H_{401}(\text{transition}) = 1400 \text{ cal/mol}$$
$$C_p(KNO_3, \beta) = 28\cdot80 \quad (401\text{–}611°K)$$
$$\Delta H_{611}(\text{fusion}) = 2800 \text{ cal/mol}$$
$$C_p(KNO_3, l) = 29\cdot50 \quad (611\text{–}700 °K)$$
$$C_p(NO_2, g) = 10\cdot7 + 2\cdot28 \times 10^{-3}\,T - 1\cdot67 \times 10^5\,T^{-2} \quad (298\text{–}2000°K)$$
$$C_p(O_2, g) = 7\cdot16 + 1\cdot00 \times 10^{-3}\,T - 0\cdot40 \times 10^5\,T^{-2} \quad (298\text{–}3000°K)$$
$$C_p(K, s) = 1\cdot34 + 19\cdot40 \times 10^{-3}\,T \quad (298\text{–}336\cdot4 °K)$$
$$\Delta H_{336\cdot4}(\text{fusion}) = 558 \text{ cal/mol}$$
$$C_p(K, l) = 7\cdot06 + 0\cdot70 \times 10^5\,T^{-2} \quad (336\cdot4\text{–}1100°K)$$
$$\Delta H^\circ_{f\,298\cdot16}(KNO_3) = -117\cdot76 \text{ Kcal/mol}$$
$$\Delta H^\circ_{f\,298\cdot16}(NO_2) = 8\cdot091 \text{ Kcal/mol}$$
$$\Delta G^\circ_{f\,298\cdot16}(KNO_3) = -93\cdot96 \text{ Kcal/mol}$$
$$\Delta G^\circ_{f\,298\cdot16}(NO_2) = 12\cdot390 \text{ Kcal/mol}$$

enthalpy of change of state of the substances involved in reaction (2) are available in the literature.[5,6] The required thermodynamic data have been compiled in Table 2. Following the known method of calculation,[7] the free energy of formation of potassium nitrate at $T°K$ for unit activity of the components of reaction (2) was computed. The following equation was deduced to express the standard emf, $E°$, in V, of cell I:

$$E° = 5\cdot440 + 3\cdot812 \times 10^{-4}T \ln T - 6\cdot231$$
$$\times 10^{-8}T^2 + 2\cdot623/T - 5\cdot156 \times 10^{-3}T. \tag{3}$$

To compare the figures of $E°$ given by (3) with the experimental results, the latter should be corrected for the partial gas pressures in the electrode compartment,

TABLE 3. STANDARD EMF

Temp °C	T °K	$E°_{exp}$ V	$E°_{calc}$ V
344 ± 0·5	617	3·741 ± 0·010	3·750
		3·751	3·750
354	627	3·732	3·726
		3·732	3·726
355	628	3·723	3·724
365	638	3·704	3·700
		3·694	3·700
375	648	3·695	3·676
380	653	3·675	3·664

whereas the activity of potassium nitrate, as well as that of potassium itself, is considered unity. Thus,

$$(E°)_{exp} = E - \frac{RT}{F} \ln p_{NO_2} p_{O_2}^{1/2}. \tag{4}$$

Considering the magnitude of the dissociation constant of nitrogen dioxide at temperature T[8] and the composition of gas mixture, we may reasonably state as a first approximation, $p_{NO_2} = \frac{2}{3}$ and $p_{O_2} = \frac{1}{3}$. Values from (3) and (4) are assembled in Table 3. The agreement may be considered quite satisfactory.

Besides providing a new galvanic cell with a nitrate electrode, these results show the possibility of forming a reliable potassium/potassium-ion reversible electrode, which allows interesting applications in fused salt electrochemistry.

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