

REACTION OF NICKEL(II) AND PERCHLORATE IONS IN FUSED LITHIUM PERCHLORATE

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Reaction of nickel(II) and perchlorate ions in the medium of fused lithium perchlorate in the temperature range 275–310°C was studied at the nitrogen flow rate 50–150 ml/min. The interpretation of experimental data was suggested in terms of two kinetic equations from which the respective values of rate constants were calculated. The values of activation energies were determined to be 28.5 and 43 kcal/mol.

Decomposition of alkali metals perchlorates was followed by Markowitz¹, Solymosi² and a number of other authors who found that in the absence of acceptors of oxygen ions the only decomposition products are oxygen and the respective chloride. The effect of substances acting as oxygen acceptors was studied by Solymosi²⁻⁵ and Acheson⁶ who followed the reaction of silver, zinc and cadmium ions with alkali metals perchlorates in the solid phase. The results of their measurements indicate that in this case the decomposition products are oxygen, chlorine, chlorides and oxides of the respective metals. Reaction of nickel(II) ions with perchlorate anions has not hitherto been studied and the only data available are those in the paper of Georgescu and Vilcu⁷ who found, in investigating the thermal decomposition of nickel perchlorate that this reaction proceeds in the solid state phase at temperatures 110°C and higher under the formation of oxygen, nickel(II) oxide, chlorine and nickel(II) chloride.

The aim of the present work was to determine the course of the reaction of nickel(II) with perchlorate in a melt of lithium perchlorate, further to study the effect of various factors on this reaction, and finally to propose a kinetic relation describing the studied process.

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EXPERIMENTAL

Chemicals

Anhydrous nickel(II) perchlorate was prepared from nickel(II) hydroxide and from perchloric acid, both of reagent grade purity (Lachema). The product was twice crystallized and dried on air for six hours at 100°C.

Lithium perchlorate was prepared analogously from lithium hydroxide and perchloric acid, also both of reagent grade purity. The formed lithium perchlorate was after crystallisation dried first for 10 hours at 170°C and then for 10 hours at 245°C. Afterwards the product was fused and at about 270°C it was treated with a few drops of perchloric acid. The lithium perchlorate prepared in this way contained no detectable amount of chlorides and the solution after melting was colourless and clear.

Procedure

The reaction mixture was placed in a quartz test tube, equipped with a device for pouring in solid samples and with an inlet and outlet for nitrogen. Nitrogen was fed to the bottom of the test tube and it served for complete mixing of the melt as well as for removing all the gaseous products. The test tube was placed in a heated brass block which was maintained at constant temperature within an accuracy better than $\pm 0.5^\circ\text{C}$. Nitrogen, along with the gaseous reaction products was then fed into an equipment which allowed to register the total amount of released chlorine. This equipment was described in our preceding publications⁸.

Concentration of nickel(II) salts was calculated from the amount of chlorine released. The plausibility of this method was demonstrated by the constant value of the molar ratio of the released chlorine to the initial weighed amount of nickel(II) ions. The proof was carried out simultaneously in a parallel experiment by following the concentration of nickel(II) ions by means of EDTA retitration.

The reaction was initiated, after removing air from the test tube by a stream of nitrogen, by throwing in a calculated amount of nickel(II) perchlorate and by switching the recording equipment.

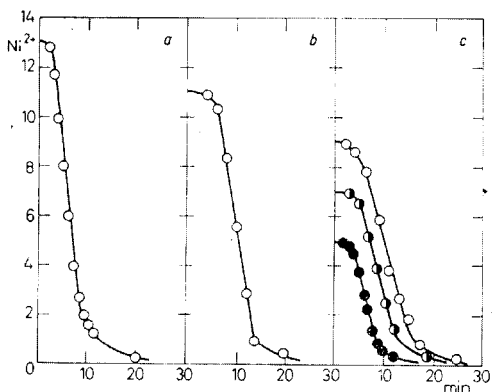


FIG. 1

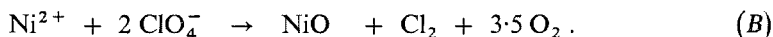
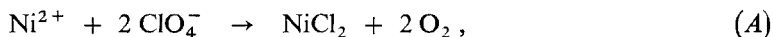
Dependence of the Reaction Rate on the Concentration of Ni^{2+} Ions

$[\text{Ni}^{2+}]$ in $\text{mol/kg} \cdot 10^3$, temperature 296°C , flow rate of N_2 150 ml/min, initial concentration of Ni^{2+} (mol/kg) a $13 \cdot 10^{-3}$, b $11 \cdot 10^{-3}$, c $9 \cdot 10^{-3}$, $27 \cdot 10^{-3}$, $35 \cdot 10^{-3}$.

RESULTS AND DISCUSSION

Products of the studied reaction, as determined analytically, are chlorine, chlorides, oxygen and nickel(II) oxide which separates in the form of very fine precipitate. This precipitate is only sparingly soluble in acids. Identification of the oxide was carried out by X-ray diffraction.

To verify the stoichiometry of the reaction we applied the equations as proposed by Georgescu and Vilcu⁷



With respect to the fact that nickel(II) chloride could not be detected at the end of the reaction, we can assume that the reaction proceeds according to equation (B). This assumption was, moreover, supported by the found molar ratio of the released chlorine to the amount of nickel(II) ions which equals $1 : 1 \pm 10\%$.

Further, the amount of the released oxygen was followed both volumetrically and by measuring the concentration of oxygen in an inert gas, after removing chlorine,

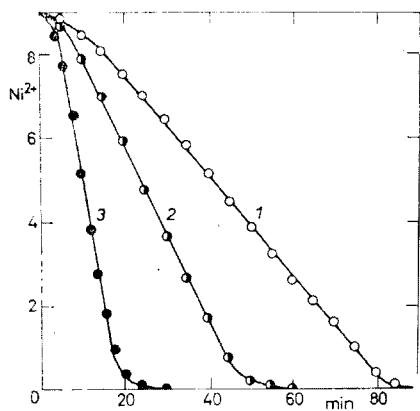


FIG. 2

Dependence of the Reaction Rate on Temperature

$[\text{Ni}^{2+}]$ in $\text{mol/kg} \cdot 10^3$, temperature ($^{\circ}\text{C}$):
 1 275, 2 285, 3 295. Flow rate of N_2 150 mol/min. initial concentration of Ni^{2+} $9 \cdot 10^{-3}$ mol/kg.

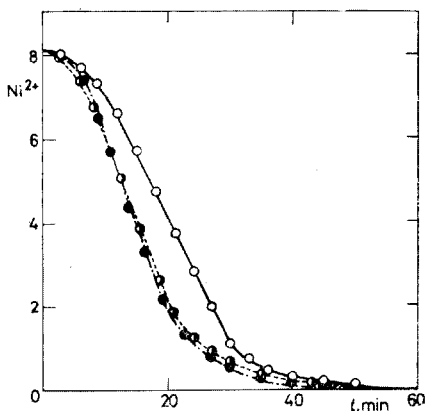


FIG. 3

Dependence of the Reaction Rate on Temperature, Repeated Experiment

$[\text{Ni}^{2+}]$ in $\text{mol/kg} \cdot 10^3$, temperature 290°C
 flow rate of N_2 150 ml/min, initial concentration of Ni^{2+} $8.1 \cdot 10^{-3}$ mol/kg, 1 starting experiment, 2 first repeated experiment, 3 second repeated experiment.

by means of Beckmann oxygen analyzer. From these measurements it follows that oxygen is released in an nonstoichiometric and irreproducible amount, according to the reaction conditions used which is probably due to the decomposition of lithium perchlorate, catalyzed either by the formed nickel(II) oxide or by some of the reaction intermediates. This assumption was proved by the fact that no chlorides were analytically determined in the reaction mixture.

When studying the effect of reaction products on the reaction course it was found that addition of chlorides diminished the reaction rate 3–5 times, whereas addition of nickel(II) oxide had no detectable effect.

The dependence of the reaction on transport phenomena was also followed. As first we studied the dependence of the reaction course on the area of the liquid-gaseous phase interphase boundary.

Different interphase areas were realized by changing the surface areas of the melt and by different flow rate of the inert gas which was varied in the range 50–150 ml nitrogen/min. The results show that the deviations lie within the limits of experimental errors. Also the measurement of the dependence of the reaction course on the area of the liquid-solid phase interphase boundary showed that the reaction does not depend on this parameter. The change of the interphase boundary was realized in this case by addition of lithium chloride. All these measurements indicate that the reaction is independent of transport phenomena.

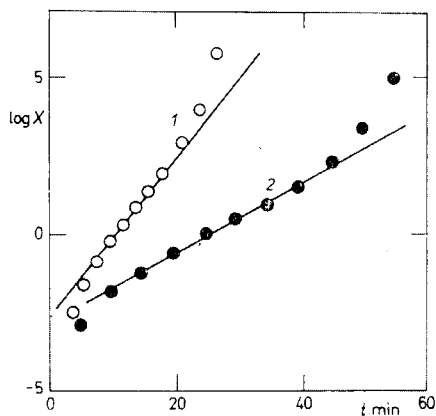


FIG. 4

Dependence of X on Time

$X = [\text{Ni}^{2+}]_t / [\text{Ni}^{2+}]_0$, temperature ($^{\circ}\text{C}$): 1 295, 2 285, flow rate of N_2 150 ml/min, initial concentration of Ni^{2+} $9 \cdot 10^{-3}$ mol/kg.

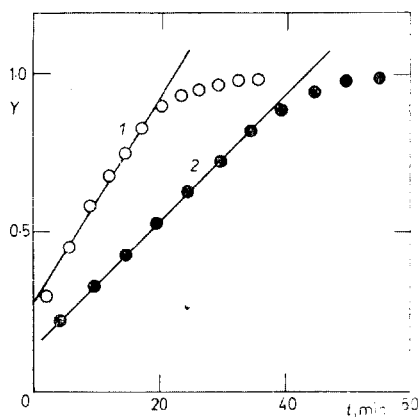


FIG. 5

Dependence of Y on Time

$Y = ([\text{Ni}^{2+}]_t / [\text{Ni}^{2+}]_0)^{1/2}$, temperature ($^{\circ}\text{C}$): 1 295, 2 285, flow rate of N_2 150 ml/min, initial concentration of Ni^{2+} $9 \cdot 10^{-3}$ mol/kg.

TABLE I

Temperature Dependence of Rate Constants according to Eqs (1) and (2) and the Respective Activation Energies

$t, ^\circ\text{C}$	$k_1 \cdot 10^3, \text{s}^{-1}$	$k_2 \cdot 10^4, \text{s}^{-1}$
275	3.9	5.3
280	2.7	4.2
285	1.8	3.3
290	1.4	2.6
295	1.0	2.1
$E_A, \text{kcal/mol}$	43.0	28.5

The course of the kinetic dependence which has the characteristic S-shape with a linear central part, is evident from Fig. 1. The dependence of the reaction rate on the initial concentration of nickel(II) ions reveals (Fig. 1) that at low concentrations, $5-9 \cdot 10^{-3} \text{ mol/kg}$ it is independent of the initial concentration of nickel(II) ions, whereas at concentrations higher than $9 \cdot 10^{-3} \text{ mol/kg}$ it increases. The dependence of the reaction rate on temperature (Fig. 2) which was also measured, is in accordance with the Arrhenius relation. This made it possible to calculate the activation energies. Their values (Table I) support the already mentioned assumption that the reaction is independent of transport phenomena.

When the reaction was repeated with a melt, containing the product of the preceding experiment (Fig. 3), it was found that the first repeated experiment had a greater reaction rate than the initial experiment, however, the total time of reaction remained unchanged. The second and further repeated experiments do not differ from the first repeated one. We did not find any explanation of this phenomenon.

There are three possibilities how to interpret the found kinetic course of the reaction. 1) Autocatalysis by reaction intermediates, 2) a system of consecutive reactions, 3) autocatalysis by reaction products. In our case autocatalysis by reaction intermediates can be excluded, since the kinetic course of the reaction does not change upon addition of a small amount of the melt from the preceding experiment to the react on mixture. Also the system of consecutive reactions is not plausible because in such a case repeated experiments in the same melt should be identical. The third possibility, *i.e.* autocatalysis by reaction products, can be admitted assuming that nickel(II) oxide can be effective. Nickel(II) oxide is formed at the beginning of the reaction and its amount are proportional to the amount of the reacted nickel(II) ions. The respective kinetic equation has the following form

$$\log \left(\frac{[\text{Ni}^{2+}]_t}{[\text{Ni}^{2+}]_0} \right) = k_1 t + C_1 \quad (1)$$

This equation is formally in accordance with the Prout-Tompkins relation for autocatalysis, as used in heterogeneous kinetics. As can be seen from Fig. 4, this equation does not hold completely for the whole extent of the reaction, nevertheless, it gives a picture of the reaction course.

The formal agreement with the equation used in the kinetics of heterogeneous reactions made us to test the validity of other equations used in this field. Fig. 5 shows how the reaction proceeds according to a simple power relation

$$([\text{Ni}^{2+}]_t/[\text{Ni}^{2+}])^{1/2} = k_2 t + C_2. \quad (2)$$

As it is evident this equation is valid nearly from the beginning up to the values of the degree of decomposition 0.6. The values of activation energies were calculated from kinetic constants, corresponding to equations (1) and (2). The results are summarized in Table I.

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