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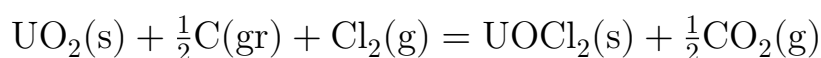
Abstract

Full Text

PHYSICAL CHEMISTRY

M. V. SMIRNOV; I. F. NICHKOV, S. P. RASPOPIN and M. V. PERFIL' EV

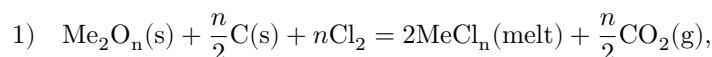
STUDY OF THE THERMODYNAMICS OF THE REACTION



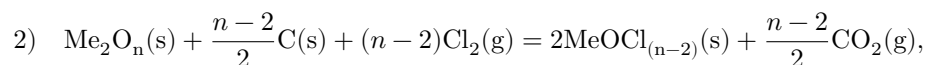
BY THE METHOD OF ELECTROMOTIVE FORCES

(Presented by Academician V. I. Spitsyn on 19 IX 1959)

In previous works (¹⁻³) it was established that oxide-carbon electrodes pressed from intimate mixtures of metal oxides and carbon are reversible with respect to the corresponding cations in chloride melts. This makes it possible to use them for studying the thermodynamics of certain reactions by the e.m.f. method (⁴⁻⁶). These include, in particular, chlorination reactions of two types:



when the oxide does not interact appreciably with the metal chloride in the melt, as occurs, for example, in the case of oxide-carbon electrodes of beryllium, calcium, and thorium, and



when the oxide forms with the chloride an oxychloride insoluble in the melt.

The possibility of applying this method to the study of the thermodynamics of chlorination reactions of the second type was tested by us using uranium oxide-carbon electrodes containing its dioxide as an example. It is known (⁷) that at 600° and above it interacts with a melt of the tetrachloride, forming the oxychloride UOCl_2 . There is no information in the literature concerning the relative solubility of this compound in chloride melts. However, in one of our works (⁸) it was established that thorium oxychloride, ThOCl_2 , is practically insoluble in chloride and mixed fluoride-chloride melts. It could be expected that the oxychloride of tetravalent uranium should possess an analogous property.

If this is so, uranium oxide-carbon electrodes containing the dioxide in their composition should absorb uranium tetrachloride from the melt until its concentration reaches the value corresponding to the equilibrium:

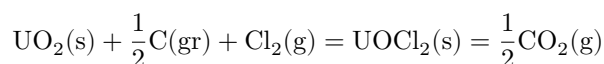


It is quite obvious that the equilibrium potential of the oxide-carbon electrodes established with time is determined precisely by this concentration and should not depend on the initial content of tetrachloride in the melt, nor on the ratio of oxide to carbon in the electrode mass. At the same time, however, it must be borne in mind that, as a result of the difference in the specific gravities of uranium dioxide and oxychloride, the electrodes may disintegrate, and the more so the larger the amount of tetrachloride they absorb. Such disintegration of electrodes due to the formation of oxychlorides was observed by us ⁽¹⁾ in the case of thorium, when the melts contained more than 25 wt.% ThCl_4 .

Thus, by combining uranium oxide-carbon electrodes ($\text{UO}_2 + \text{C}$) with a chlorine electrode in melts of alkali-metal chlorides containing uranium tetrachloride, and by measuring the temperature dependence of the e.m.f. of such elements:



one can find the change in the isobaric potential ΔZ for the reaction:



$$\Delta Z = -46124 \cdot \varepsilon \text{ cal/mole UOCl}_2.$$

The oxide-carbon electrodes were prepared from uranium dioxide, which was obtained by calcining the peroxide in air at 600° . The fine powder thus formed was mixed in the required proportions with sugar syrup and evaporated until a powdery mass formed; from this mass, cylinders 10 mm in diameter and 5–15 mm long were pressed under a pressure of 4000 kg/cm^2 . They were fired without access of air under a layer of coal, gradually raising the temperature to 800° . In this process the uranium dioxide was reduced by carbon. Analysis of the fired electrodes showed that they contained uranium dioxide whose composition varied from $\text{UO}_{2.02}$ to $\text{UO}_{2.06}$, and free carbon in an amount sufficient to bind all the oxygen into CO_2 . In individual experiments the molar ratio of dioxide to carbon was deliberately varied over wide limits from 1 : 1.6 to 1 : 200. The electrodes were attached to current leads made of spectrally pure carbon.

Fig. 1. Cell. 1—quartz test tube; 2—thermocouple; 3—molybdenum current lead to the lead electrode; 4—carbon current leads; 5—oxide-carbon electrodes; 6—molten lead; 7—electrolyte

The electrolyte used was either a molten eutectic mixture of lithium and potassium chlorides ($t_m = 352^\circ$), or a molten equimolar mixture of sodium and potassium chlorides ($t_m = 662^\circ$), in which uranium tetrachloride was dissolved. It was prepared by chlorinating uranium dioxide with carbon tetrachloride at 500° in a stream of pure argon. The sublimed tetrachloride was purified by repeated sublimation in vacuum at 700° . The arrangement of the cell in which the measurements were carried out is shown schematically in Fig. 1. A lead electrode was used as the reference electrode; it was located in a separate test tube filled with molten eutectic LiCl and KCl with an addition of 8 wt. % PbCl_2 . In specially conducted experiments the temperature dependence of the e.m.f. between the lead and chlorine electrodes was found. Taking into account the thermoe.m.f. between the carbon rod of the chlorine electrode and the molybdenum current lead to the lead electrode, it is expressed by the empirical equation

$$\varepsilon = (1.639 - 3.04 \cdot 10^{-4}T) \text{ V.}$$

Before the experiments, the salt melt in the cell was purged with dry hydrogen chloride to remove possible hydrolysis products, and then kept under vacuum to remove dissolved gases from it. The space above the electrolyte was filled with an equilibrium mixture $\text{CO}_2 + \text{CO}$, which was obtained by passing carbon dioxide through a tube with finely divided carbon heated to the experimental temperature ($\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$). The cell was placed...

was carried out in a massive metal block heated in an electric resistance furnace with automatic temperature control, which could be maintained at a specified value with a constancy of $\pm 2^\circ$. The e.m.f. between the oxide-carbon and lead electrodes of the cell was measured with a high-resistance potentiometer over a long period of time, until it reached a constant value (changing over the course of an hour by no more than ± 3 mV).

The established equilibrium values of the e.m.f. did not depend on the initial content of uranium tetrachloride in the melt or on the quantitative ratio of uranium dioxide to carbon in the electrodes, and were determined only by temperature. However, these factors had a substantial effect on the change in the cell e.m.f. during the establishment of equilibrium. Equilibrium values were reached the more quickly, the less uranium tetrachloride had been taken and the higher the temperature was. Other conditions being equal, the potential of electrodes with a higher carbon content (which were more porous) was established more rapidly. This can be illustrated by the results of several experiments, which are shown graphically in Fig. 2.

Fig. 2. Change in the cell e.m.f. with time.

1—in a LiCl–KCl melt containing 0.93 wt.% UCl_4 ; molar ratio $\text{UO}_2 : \text{C} = 1 : 1.6$.
2—taken in a LiCl–KCl melt containing 2.0 wt.% UCl_4 ; molar ratio $\text{UO}_2 : \text{C} = 1 : 200$.

When the melt contained large amounts of uranium tetrachloride, considerable

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Figure 1: Fig. 2. Change in the cell e.m.f. with time. 1—in a LiCl–KCl melt containing 0.93 wt.% UCl_4 ; molar ratio $\text{UO}_2:\text{C} = 1:1.6$. 2—taken in a LiCl–KCl melt containing 2.0 wt.% UCl_4 ; molar ratio $\text{UO}_2:\text{C} = 1:200$

Fig. 3. Temperature dependence of the equilibrium values of the e.m.f. of the cell $\text{UO}_2 + \text{C} + \text{UOCl}_2/\text{LiCl}, \text{KCl}, \text{UCl}_4/\text{Cl}_2, \text{C}$

Figure 2: Fig. 3. Temperature dependence of the equilibrium values of the e.m.f. of the cell $\text{UO}_2 + \text{C} + \text{UOCl}_2/\text{LiCl}, \text{KCl}, \text{UCl}_4/\text{Cl}_2, \text{C}$

destruction of the oxide–carbon electrodes was observed, up to their complete “dissolution,” before the equilibrium potential was reached. At a relatively low content of UCl_4 in the electrolyte the electrodes were destroyed only slightly. An equilibrium potential was established on them and subsequently they underwent no appreciable changes, similar to electrodes immersed in a melt of alkali-metal chlorides without the addition of uranium tetrachloride. Establishment of the equilibrium e.m.f. corresponds to attainment of equilibrium:



Fig. 3. Temperature dependence of the equilibrium values of the e.m.f. of the cell $\text{UO}_2 + \text{C} + \text{UOCl}_2/\text{LiCl}, \text{KCl}, \text{UCl}_4/\text{Cl}_2, \text{C}$

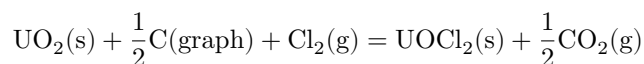
Analysis of the solidified electrolyte showed that the equilibrium concentration of uranium tetrachloride amounts to several thousandths of a percent in the temperature range we investigated, 600–900°. The temperature dependence of the equilibrium e.m.f. values was measured with electrolytes containing not more than 6 wt.% UCl_4 . It should be noted that, after the equilibrium concentration of uranium tetrachloride had been established in the electrolyte, the e.m.f. followed changes in temperature considerably more rapidly. The measurement results, recalculated relative to the chlorine electrode, are presented graphically in Fig. 3.

The experimental points lie on a straight line described by the empirical equation:

$$\varepsilon = (0.713 + 4.8 \cdot 10^{-4}T) \text{ V}.$$

As already stated above, this quantity is a direct measure of the change in the isobaric potential for the reaction of interest to us.

chlorination:



$$\Delta Z = (-32900 - 2.2T) \text{ cal/mole UOCl}_2.$$

Consequently, the thermal effect of this reaction is $\Delta H = -32.9$ kcal/mole UOCl_2 , and the entropy is $\Delta S = 2.2$ cal/deg · mole UOCl_2 .

On the basis of the thermodynamic data available in the literature ⁽⁹⁾, from the value of ΔZ found by us one can calculate the standard values of the heat of formation and entropy of uranium oxychloride:

$$\Delta H_{\text{UOCl}_2}^0 = \Delta H + \Delta H_{\text{UO}_2}^0 - \frac{1}{2}\Delta H_{\text{CO}_2} =$$

$$= 32900 - 270000 + \frac{1}{2}94000 = -255900 \text{ cal/mole};$$

$$S_{\text{UOCl}_2}^0 = \Delta S + S_{\text{UO}_2(\text{s})}^0 + \frac{1}{2}S_{\text{C}(\text{graph})}^0 + S_{\text{Cl}_2(\text{g})}^0 - \frac{1}{2}S_{\text{CO}_2(\text{g})}^0 =$$

$$= 2.2 + 18.6 + \frac{1.4}{2} + 53.3 - \frac{51.1}{2} = 49.2 \text{ cal/deg} \cdot \text{mole}.$$

In the literature ⁽⁷⁾, the following values are given for the thermodynamic constants of the oxychloride: $\Delta H_{298}^0 = -261.7$ kcal/mole and $S_{298}^0 = 38.1$ e.u. As can be seen, within the assumptions made in the calculations and the possible errors of measurement, there is quite satisfactory agreement in the values of the heat of formation, but a rather large discrepancy in the entropy values. It is possible that the latter is connected with peculiarities of the structure of uranium oxychloride formed under the conditions of our experiments.

Thus, this indicates the acceptability of the method of electromotive forces with oxide-carbon electrodes for studying the thermodynamics of chlorination reactions leading to the formation of oxychlorides.

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