

THERMODYNAMIC FUNCTIONS OF SUBSTOICHIOMETRIC URANATES FROM CLOSED-COMPARTMENT GALVANIC CELL MEASUREMENTS

D.JAKEŠ

*Institute of Nuclear Research,
Czechoslovak Academy of Sciences, Prague-Řež*

PE 128 / 38.1973.1-3.

Received November 16th, 1971

Equilibrated samples of highly substoichiometric magnesium, calcium, strontium and barium monouranates were used in testing a closed-compartment, high-temperature galvanic cell device. The partial enthalpies and entropies were determined with a high accuracy. Coulometric and stability examinations demonstrated the reliability and reproducibility of the proposed design.

The chemistry of nonstoichiometric ionic crystals presents certain new problems. The experimental as well as theoretical requirements become rather complicated with large departure from stoichiometry. The configuration of the crystal lattice becomes indefinite¹ and more than one type of the unit cell can be proposed. The main effort then concentrates on finding out the mode how the deviation from stoichiometry is incorporated into the crystal. The common X-ray analysis must be supplemented by a thermodynamic equilibrium method, especially if high temperatures are concerned. The measurement of galvanic cells with solid electrolytes is one of the most suitable methods. With highly nonstoichiometric ionic crystals, the design of galvanic cells after Kiukkola and Wagner^{2,3}, or Steele^{4,5} has to be modified. Sometimes the interpretations of crystallographic and thermodynamic measurements are controversial. Structural analysis tends rather to interpret wider homogeneity limits of nonstoichiometric ionic crystals in terms of a series of crystallographically related crystal lattices with a narrower range of homogeneity. On the other hand, thermodynamic measurements lead to the assumption that the ionic crystals have wide ranges of homogeneity. To decide between these alternatives, better techniques with a higher "resolving power" must be applied.

The present work deals with a completed galvanic cell in a so-called closed-compartment arrangement and its testing with the aid of highly nonstoichiometric monouranates of alkaline earth metals. The design of the apparatus is based on requirements following from the specific character of nonstoichiometric ionic crystals, similar to thermodynamic measurements of homogeneous solid solutions. Namely, all thermodynamic quantities can be expressed as partial functions of composition, in our case concentration of oxygen in the crystal. In other words, the studied quantities will be strongly dependent on the concentration of active components of the ionic crystal in the surrounding medium⁶.

The present work concerns mainly the reliability and the reproducibility of the measurement for the purpose of the study of the thermodynamics of ternary non-

stoichiometric oxides rather than the study of the complete phase diagram of mono-uranates in the range from $MU^{VI}O_4$ to $MU^{IV}O_4$.

EXPERIMENTAL

The galvanic cell (Fig. 1) was placed in a hermetic alumina tube (Morgan Ltd.) which was held in a brass head equipped with necessary fittings for thermocouple and galvanic cell leads. This cap held also the tubing for flushing the hot zone with argon and for air-circulation eventually used in the reference electrode. The composition of the controlled atmosphere could be maintained constant for months. The hermetic tube was enclosed in an earthed thin nickel foil (0.05 mm) to screen spurious outside electric fields. The temperature was controlled by an electronic regulator (Eurotherm Ltd.) with a Pt/PtRh thermocouple (13% Rh). The stability was better than $\pm 1^\circ\text{C}$.

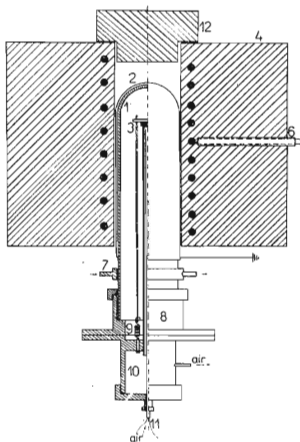


FIG. 1

Experimental Setup for Measurement with Solid Electrolytes

1 Alumina tube; 2 screening nickel foil; 3 closed-compartment galvanic cell (Fig. 2); 4 thermal insulation; 5 heating coil; 6 thermocouple; 7 cooling ring; 8 brass head with electric connections and inlet and outlet of argon; 9 spring; 10 air chamber in the brass head; 11 thermocouple; 12 insulation brick.

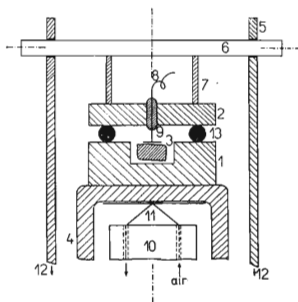


FIG. 2

Closed-Compartment Galvanic Cell

1 Solid electrolyte ($ZrO_2 + 8 \text{ mol } \% Y_2O_3$) with central well; 2 alumina lid; 3 sample; 4 solid electrolyte tube; 5 alumina pulling rods; 6 alumina cylindrical rod; 7 alumina supporting ring; 8 Pt contact; 9 glass seal; 10 thermocouple ceramic capillary; 11 thermocouple; 12 pull direction.

The galvanic potential was measured alternately by a vibration electrometer Vibron 33-B (input resistance 10^{13} ohm) and a digital voltmeter Solartron (input resistance 10^9 ohm). The temperature in the compartment of the galvanic cell was measured by a Pt/PtRh thermocouple (13% Rh) with a Tinsley compensating bridge.

The design of the closed-compartment galvanic cell based on the published system^{7,8} is shown in Fig. 2. The solid electrolyte was a solution of 8 mol % Y_2O_3 in ZrO_2 of spectral purity (Johnson-Matthey; maximum impurities 10 p.p.m.). It was prepared by dissolving the oxides in nitric acid (Analar reagent, Hopkins and Williams), drying, calcining at $400^\circ C$, grinding in a mechanical agate mortar, pressing into pellets (7 Mp/cm^2) and sintering in a tungsten resistance furnace in a thoria crucible for 5 h at $1800^\circ C$. Small central wells were drilled into the sintered pellets by ultrasonic drill. Both bases of the pellets were polished with a wet SiC paper (final grade 600) and washed with organic solvents. The upper platinum contact was fixed in the hole of the alumina lid by means of crystalline glass^{9,10}. This seal behaved satisfactorily and was after a prescribed thermal treatment stable up to $1350^\circ C$.

The basic components of the galvanic cell, the electrolyte pellets provided with the well and the alumina lid with the contact were after inserting a sample into the well joined and sealed with a ring-shaped gold wire. In some cases a higher-melting Au-Pd alloy was substituted for gold enabling measurements at a higher temperature (up to $1200^\circ C$). After heating in the furnace pressed together with spring-loaded alumina rods, the components of the compartment isolation of the sample were joined so firmly that they could be separated only by amalgamation of the golden seal with hot mercury overnight. Alumina pulling rods similar to those proposed by Steele^{4,5} were used (Figs 1, 2). The complete setup was inserted into the ceramic tube, which was sealed, evacuated to 10^{-5} Torr and outgassed at $300^\circ C$ to prevent possible uncontrolled reduction of the measured, previously calibrated sample. After the vacuum had been reestablished, the temperature was raised to $950^\circ C$; after about 5 h the compartment of the measured electrode was sealed off (with the Au-Pd seal, a higher temperature was necessary). The tube was then slowly filled with argon and a constant gas flow was established. The argon was purified by passing over copper or iron at $700^\circ C$, the partial pressure of oxygen being thus reduced to 10^{-5} or 10^{-10} atm.

The uranate sample was prepared for measurement by reduction with a gas buffer or a controlled atmosphere until equilibrium was reached under chosen partial pressure of oxygen. The apparatus (used also in measuring gas-solid phase equilibria) was described elsewhere^{11,12}. The actual measurement was made with 10–20 μg of the sample. The nonstoichiometric samples were perfectly sintered and were insensitive towards oxidation with air. Monouranates of magnesium, calcium, strontium and barium were prepared by long-term heating at $1000^\circ C$ of a finely ground mixture of U_3O_8 and the corresponding oxides of spectral purity (Johnson-Matthey) in oxygen

TABLE I

Partial Enthalpies and Entropies of Oxygen Dissolution in Substoichiometric Uranate Lattice

Compound	$\Delta \bar{H}_T$, kJ/mol O	$\Delta \bar{S}_T$, J/K mol O
MgUO _{3.667} ± 0.001	-17.083 ± 0.05	-9.27 ± 0.1
CaUO _{3.884} ± 0.001	-16.318 ± 0.05	-8.24 ± 0.1
SrUO _{3.768} ± 0.001	-14.395 ± 0.05	-6.28 ± 0.1
BaUO _{3.670} ± 0.001	-11.508 ± 0.05	-5.16 ± 0.1

atmosphere. The solid-state reaction was accelerated by grinding from time to time in a mechanical agate mortar. The purity of the products was checked by the X-ray powder diffraction method until the reflections of the free oxides including U_3O_8 disappeared (sensitivity of the determination about ± 7 weight %). In addition, the disappearance of black-green particles of U_3O_8 , clearly visible on the yellow-orange background of uranates, was checked microscopically. The composition of the uranates was determined by chemical analysis and the stoichiometry of oxygen by heating in a stream of oxygen and weighing on a microbalance.

A millivolt recorder (Honeywell) was used as a charge integrator in coulometric titrations. A dry battery with a potentiometer served as a source of d.c. voltage. The duration of one titration was 3–4 days, the overvoltage was normally 20 mV. An oxygen reference electrode was fed with air passing slowly through the electrolyte tube, which was made of sintered zirconia stabilized by yttria (Zircoa, U.S.A.). The contact surface between both electrolytes was polished to decrease the contact resistance. The advantage of the air electrode against electrodes with a solid depolarizer is that it does not contaminate the electrolyte.

RESULTS AND DISCUSSION

From the measured values of the electromotive force (Fig. 3) as a function of temperature, the partial enthalpy and entropy were calculated. The calculations were based on the Nernst equation

$$E = (RT/nF) \ln p_{O_2}, \quad (1)$$

modified Gibbs–Helmholtz equation

$$-\Delta\bar{S}_T = (\partial\Delta\bar{G}_T/\partial T)_p = -nF dE/dT \quad (2)$$

and equation of van't Hoff isobar

$$\Delta\bar{H}_T = RT^2(d \ln p_{O_2}/dT) = -R[d \ln p_{O_2}/d(1/T)], \quad (3)$$

where E denotes measured galvanic potential, n number of electrons in the given electrode reaction = 4, K_p isobaric equilibrium constant of the electrochemical reaction, $\Delta\bar{G}_T$ partial free enthalpy of oxidation, $\Delta\bar{S}_T$ partial entropy of oxidation, $\Delta\bar{H}_T$ partial enthalpy of oxidation. The validity of Eqs (1)–(3) was discussed in detail previously¹³.

The quantities of interest were calculated by the least squares method, the results are in Table I. The obtained accuracy shows that the studied system is suitable for our purpose and enables to study the influence of small changes in composition on the thermodynamic functions. The linear dependence of $\log p_{O_2}$ on temperature (Fig. 3) suggests the existence of a local homogeneity region at the given composition of the ionic crystals.

In view of the considerable resistance of the studied setup (of the order of 10^4 ohm), the current in the coulometric titrations could be only 1–4 μ A. A higher current would require a higher overvoltage implying the possibility of irreversible changes on the electrolyte surface. The high resistance was probably caused by the additional electrolyte layer introduced by an electrolyte tube forming the space of the air reference electrode, and could be probably suppressed through a more perfect surface polishing.

The coulometric experiments showed also whether the closed system is hermetic. A certain amount of oxygen was transferred electrolytically into the cell to increase the concentration polarization by 25–30 mV and then it was reduced by an equivalent charge. The results showed that the electrode reaction was reversible with all uranates under study. The differences among reversibly transferred charges did not exceed $\pm 3\%$, which is quite plausible with the given arrangement.

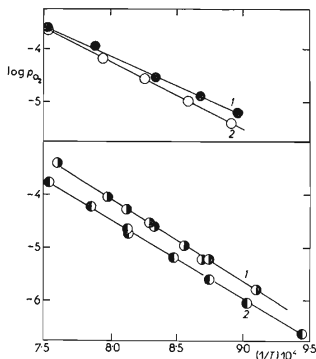


FIG. 3
Equilibrium Partial Pressure of Oxygen
in Substoichiometric Uranates as a Function
of Reciprocal Absolute Temperature
● $\text{BaUO}_{3.670}$; ○ $\text{SrUO}_{3.768}$; ● $\text{MgUO}_{3.667}$
○ $\text{CaUO}_{3.884}$.

The potential of a comparative analyzer with a solid electrolyte (pO meter¹²) in the apparatus for the preparation of the equilibrated sample was the same as the potential measured finally with the galvanic cell at the same temperature. This shows the reliability of our experimental procedure during transferring the sample from the reduction apparatus into the galvanic cell. The long-term reliability of the arrangement was also proved by heating for up to 3 months resulting in no measurable shift of the cell voltage. It follows that oxygen did not pass along the glass or gold seal and even along the interface formed by three construction components, which is most important. The difference between the partial oxygen pressure in the hermetic outer tube and in the closed-compartment well containing the sample was usually at least two orders of magnitude, but not more than four orders. With greater differences, the possibility of interfering diffusion of oxygen becomes more important.

In two experiments (with monouranates of calcium and strontium) it sometimes occurred that the cell voltage dropped in the course of several days for an unknown reason attaining a certain minimum (e.g. from 211 to 195 mV) and returning to the original value again. Then it remained constant. To elucidate this effect, studies will be made on a modified apparatus.

The author is indebted to Prof. C. B. Alcock, University of Toronto, for valuable advice and to the Science Research Council of the United Kingdom for financial support.

REFERENCES

1. Greenwood N. N.: *Ionic Crystals, Lattice Defects and Nonstoichiometry*, p. 130. Butterworths, London 1968.
2. Kiukkola K., Wagner C.: *J. Electrochem. Soc.* **104**, 308 (1957).
3. Kiukkola K., Wagner C.: *J. Electrochem. Soc.* **104**, 379 (1957).
4. Steele B. C. H.: *Thesis*. University of London, 1965.
5. Steele B. C. H.: *Proc. Nuffield Res. Group Symp.* (Inst. Min. Met.), London 1968.
6. Schottky W., Wagner C.: *Z. Physik. Chem. B* **11**, 163 (1930).
7. Zador S.: *Thesis*. University of London, 1969.
8. Zador S., Alcock C. B.: *J. Chem. Thermodynam.* **2**, 9 (1970).
9. Mukerjee S. P., Rogers P. S.: *Phys. Chem. Glasses* **8**, 81 (1967).
10. Rogers P. S., Buttler J., Steele B. C. H.: *J. Sci. Inst., Ser. 2*, **2**, 102 (1969).
11. Jakeš D., Škvor F., Dáňa J.: *Zpráva ÚJV č. 2546-M* (1970).
12. Jakeš D.: *Silikáty*, in press.
13. Jakeš D.: *Chem. listy* **63**, 1073 (1969).

Translated by K. Micka.