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A MANOSTAT VOLUMETRIC APPARATUS FOR STUDIES ON THE KINETICS OF HIGH-TEMPERATURE REACTIONS IN SOLID-GAS SYSTEMS

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A new volumetric apparatus is described for continuous measurement of the kinetics of the oxidation of metals at high temperatures, and for measurement of adsorption and chemisorption of gases on solids. The measurement of the kinetics of oxygen fixation is performed automatically with very high precision. The oxidation of copper has been used to test the performance of the apparatus.

Studies on the mechanisms of reactions in solid-gas systems, which include such processes as the thermal decomposition of solids and oxidation of metals and alloys, require the use of increasingly accurate methods of measurement [1, 2]. Kinetic measurements play an essential role in these studies. In the case of oxidation processes, for instance, these measurements at various temperatures and pressures of the oxidizing medium provide valuable information about elementary processes which, under the given conditions, control the rate of the overall reaction. In many cases they allow calculations to be made of the defect concentration and self-diffusion coefficient of a metal or an oxidant in the solid product of oxidation of a metal or an alloy.

Of the numerous methods used for studying the kinetics of the processes under discussion, two basic methods may be distinguished: a gravimetric and a volumetric method, which provide the most accurate results.

In the present paper a new volumetric apparatus is described which makes it possible to obtain very accurate values of the rate constants of reactions in the given temperature and oxygen pressure ranges.

Description of the apparatus

Due to application of a new system of manostats, the apparatus to be described enables measurements of the volume of gas consumed by a sample under isothermal-isobaric conditions to be made with high precision. All operations involved in the measurement of the reaction kinetics, with the exception of the reading of a mercury level in the measurement burette, are automatic. The range of pressures of the apparatus used in the present work was 2–600 mm Hg. It will be possible in the future to extend this range by modifying the apparatus. The work on such a modification is now in progress.

The scheme of the apparatus is shown in Fig. 1. It is composed of two basic parts of different pressures, p_1 and p_2, separated by a dosing valve 24. The first part contains a reaction tube 38 and manostat gauge 28 with a manometer. The second part comprises a measuring burette 31, connected to a manometer 27, and manostat gauge 29 and gas container 23. Both the burette and gauge 28 are connected to a mercury valve 25, the detailed construction of which was described in [3].

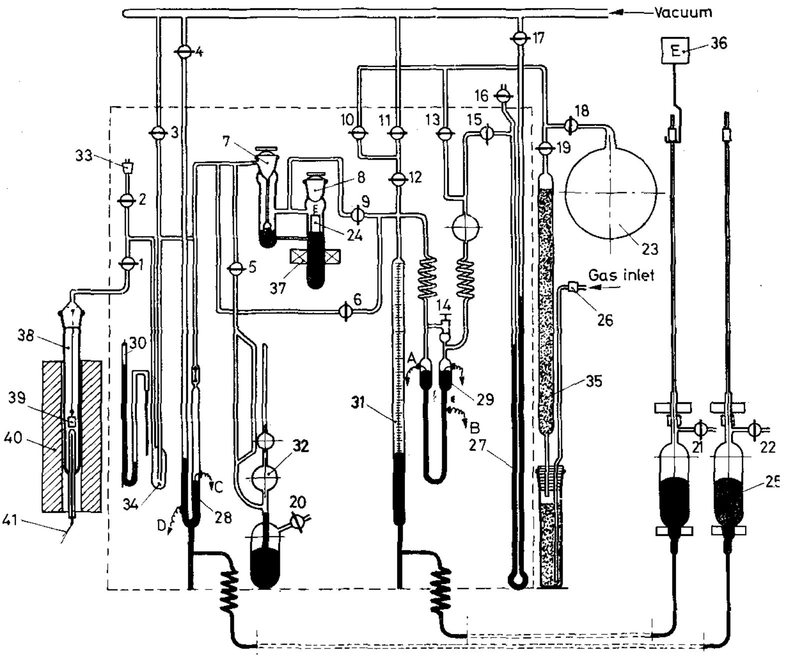

Fig. 1. Schematic diagram of manostat volumetric apparatus. 1—22 — vacuum taps, 23 — oxygen container, 24 — dosing valve, 25 — mercury valve, 26 — needle valve, 27 — manometer M_1, 28 — manometer M_2 with manostat gauge, 29 — manostat gauge, A, B, C, D — platinum wires acting as contacts with mercury, 30 — gauge maintaining constant level of refrigerant in the freezing trap, 31 — measuring burette, 32 — McLeod gauge, 33 — head of ionization gauge PJ-38, 34 — freezing trap for mercury vapour, 35 — gas purifier, 36 — electromagnet of mercury valve, 37 — electromagnet of dosing valve, 38 — reaction tube, 39 — sample, 40 — resistance oven, 41 — Pt—PtRh thermocouple

The electronic system (Fig. 2) coupled with electromagnets 36 and 37 and with platinum contacts *AB* and *CD*, which automatically maintain constant pressure in both parts of the apparatus, constitutes a separate part of the system. This pressure was measured with manometers 27 and 28 with the aid of cathetometer KM-6 with an accuracy of 0.01 mm Hg.

The principle of the measurement is as follows: after the sample has been placed in the reaction chamber, the apparatus is evacuated to the pressure of 10^{-6} mm Hg.

With the vacuum taps 1 and 3 open, the reaction space is heated to the required temperature at which the sample is maintained under continuous pumping. After heating, and checking the pressure in the reaction tube 38, taps 1 and 3 are closed. Oxygen is then admitted to the degassed remaining part of the apparatus through a system of vacuum taps 10, 12 and 18 from container 23, in such a manner as to obtain in both manostats the required pressures p_1 and p_2: after filling the measuring burette 31 with oxygen under pressure p_2 measured with a manometer 27, the electronic relay 1 (Fig. 2) is switched on. The measurement pressure p_1 is then established with the aid of valve 25, by raising the mercury to the appropriate level in manometer 28. After this operation (the taps 7 and 9 being open), the electric system of the dosing valve 24 is switched on. This valve contains two connected vessels filled with mercury. In the left-hand vessel there is a capillary with porous glass sealed at the bottom, connected to a vacuum tap 7. In the right-hand vessel, surrounded by electromagnet 37, there is a metallic core. By switching on the electromagnet the metallic core is raised, and in this way a certain amount of mercury is transferred from the left-hand vessel to the right-hand one. The porous glass is then uncovered. Oxygen from the measuring burette 31 passes through the porous glass to manometer 28, till the moment when the mercury level drops below platinum contact *C*. After the closing of vacuum tap 14 in manostat gauge 29 the initial level of mercury in the measuring burette is set with the aid of electromagnet 36.

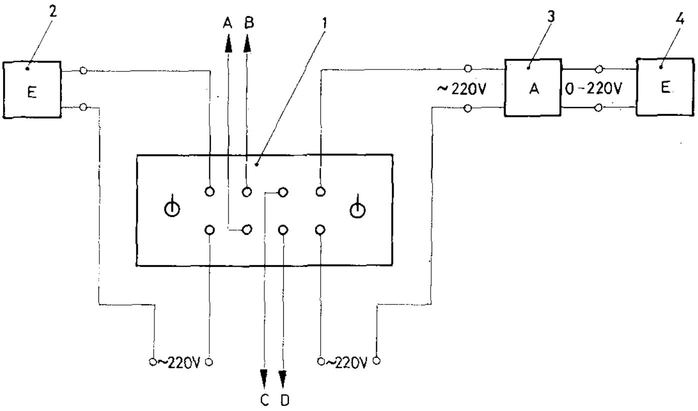

Fig. 2. Schematic diagram of electric network. 1 — electronic relay, 2 — electromagnet of dosing valve, 3 — autotransformer, 4 — electromagnet of mercury valve, A, B, C, D — platinum contacts

The experiment begins at the moment of the opening of tap 1. In the first instant a slight drop of pressure is observed, due to the increase of the measurement volume by the reaction space. This change of pressure is automatically levelled by the opening of the dosing valve 24. As the reaction proceeds, the oxygen pressure in the reaction space is slightly decreased owing to the consumption of oxygen by the sample, which causes the instantaneous rise of the mercury level in manometer 28. When the mercury level touches contact *C*, the electronic system sets in motion electromagnet 37, automatically causing the opening of the dosing valve 24. Introduction of a portion of oxygen into the reaction space leads to a pressure decrease in manostat gauge 29 and to the rise of the mercury level till it touches contact *A*. At the same time electromagnet 36 is switched on, which, by opening mercury valve 25, at the same time raises the mercury level in the measuring burette 31 stepwise till the equalization of the pressure in gauge 29. When the pressures are equalized, the electronic system ceases to operate, till the subsequent pressure drop in the reaction space. In order to avoid perturbations resulting from the volume changes in the cooled part of the apparatus, the contact gauge 30 was applied, which maintains the cooling liquid in freezing trap 34 at a constant level.

The apparatus enables continuous measurement with the exchange of any amount of oxygen in the burette. For this, after the mercury level rises to the upper limit of the measurement burette, electromagnet 36 and the electric network of the dosing valve 24 are switched off. The low-vacuum system is then connected to tap 21. By opening of the mercury valve mercury flows from the burette to the valve container. To replace the mercury in the burette, the appropriate portion of oxygen is introduced through the system of taps 12, 10 and 18, till the mercury level is equalized with platinum contact *A*. By switching on electromagnet 36 the pressure in the measuring part is automatically established at the same value p_2 as it was before filling of the burette with the new portion of oxygen. The initial level in the measuring burette is automatically set at the same time.

The measurement is continued by switching on the electric network of the dosing valve 24. The time for refilling the burette amounts to 3–4 min, which does not disturb the reaction course.

Sensitivity of the apparatus

In order to characterize the sensitivity of the apparatus in the measurements carried out at different pressures in the reaction chamber, the difference of the mercury levels, Δh_1, in manometer 28 was determined in the vicinity of contact *C* before the dosing valve was switched on and after its closing. This difference amounts on the average to 0.05 mm Hg, which constitutes only 1 % of the lowest applied pressure in the reaction chamber. Obviously, the higher the oxygen pressure in the reaction chamber, the smaller its oscillations, and thus the constant pressure in the reaction space is maintained with a higher accuracy. The volume of the oxygen portion dosed into the reaction space is $\Delta V_1 = \Delta h_1 \cdot S$, where S is the cross-sectional area of manometer 28 in the vicinity of contact *C*. In the course of the oxidation of a metal under constant pressure p_1, oxygen is dosed by the same portions $\Delta V_1 \cdot p_1$, in keeping with the following relation:

$$\Delta V_1 \cdot p_1 = \Delta h_2 \cdot a \cdot p_2 \tag{1}$$

where a is the calibration constant of the burette.

The measurement of the dosed quantity of oxygen consists in determining the difference in the mercury levels in the burette, Δh_2, caused by introduction of oxygen at a given pressure p_2 into the measurement space. The higher the pressure p_1 in the reaction space and the higher its volume, the higher should be the portions of the dosed gas. As results from relation (1), the value of Δh_2 depends on the ratio p_1/p_2. The choice of the most favourable pressure ratio is determined by the rate of the process under study. The slower the process of oxygen consumption by the sample the smaller may be the value of the pressure ratio. Pressure p_2 should be selected in such a way that the quantity of oxygen in the burette is sufficient for the fastest stage of the oxidation process, i.e. that the refilling of the burette takes place in the later, usually slower stage of the reaction. Too high a value of pressure p_2 is not recommended, since the errors in dosing large portions of gas are also high. On the other hand, if pressure p_2 were too small, introduction of a given portion of gas would require the rising of the mercury level in the burette to a considerable height (large value of Δh_2) and moreover the dosing valve would have to work too often. In this situation the mercury level in the burette would rise practically continuously, which would make accurate measurement very difficult.

From the preliminary measurements, the optimum pressure ratio p_1/p_2 was evaluated. Its value varied from 1/4 to 1/7. At such pressure ratios the introduction of the oxygen dose corresponded to a difference in the mercury levels in the burette of the order of 0.5 – 1.0 mm. In the pressure range 2 – 200 mm Hg and for calibration constant of the burette of 4.4542 ml/cm, a rise of the mercury level in the measurement burette by 0.5 mm corresponded to a consumption of $7 \cdot 10^{-7} - 7 \cdot 10^{-5}$ g of oxygen in the reaction.

Results of measurements of the kinetics of copper oxidation

In order to test the apparatus described above, the kinetics of copper oxidation at 1000° was examined at various oxygen pressures. The copper-oxygen system was selected since the kinetics of copper oxidation have recently been studied in detail by the gravimetric method using an ultra-sensitive vacuum microbalance [4]. Since these studies were performed in our laboratory it was possible to carry out the check experiments using the same material (spectrally pure copper, Johnson – Matthey product). In particular the experiments aimed at the characterization of the sensitivity of the method, the reproducibility of the results and the discussion of the errors.

According to a number of studies [4 – 8], the oxidation of copper follows the parabolic law of Pilling and Bedworth:

$$\left(\frac{\Delta m}{q}\right)^2 = k_p'' t + C \tag{2}$$

where Δm = mass of the oxidant consumed
q = surface area of the metal
t = oxidation time
k_p'' = parabolic rate constant of oxidation
C = constant

The parabolic rate constants of the oxidation were calculated using the method proposed by Mrowec and Stokłosa [9], introducing into Eq. (2) the apparent surface area of the metal q^x, which is the arithmetic mean of the initial surface area and the surface at a given instant (for a given mass of consumed oxygen Δm). This problem has been discussed in detail in [9].

Flat copper samples, 18.00 × 13.20 × 0.45 mm in size, were cut from the band obtained from cold-rolled standard copper rods 5 mm in diameter. The surfaces of the samples were polished prior to the measurement, with emery paper of decreasing gradation down to 4/0, and then washed with water, acetone and methanol.

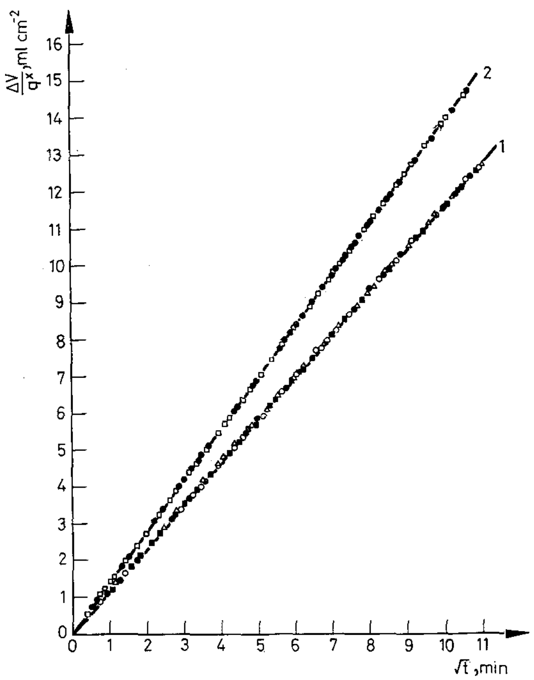

Fig. 3. Reproducibility of volumetric measurements. Results of several measurements at 1000^{C} at pressures of 10 mm Hg (curve 1) and 40 mm Hg (curve 2)

The temperature in the reaction space was maintained constant within ±5° with an electronic thermoregulator connected to a Pt—PtRh thermocouple.

The rate of copper oxidation was measured at 1000° in the pressure range 5—40 mm Hg. In agreement with the suppositions, the oxidation followed the parabolic rate law in the entire pressure range under study (Figs 3 and 4).

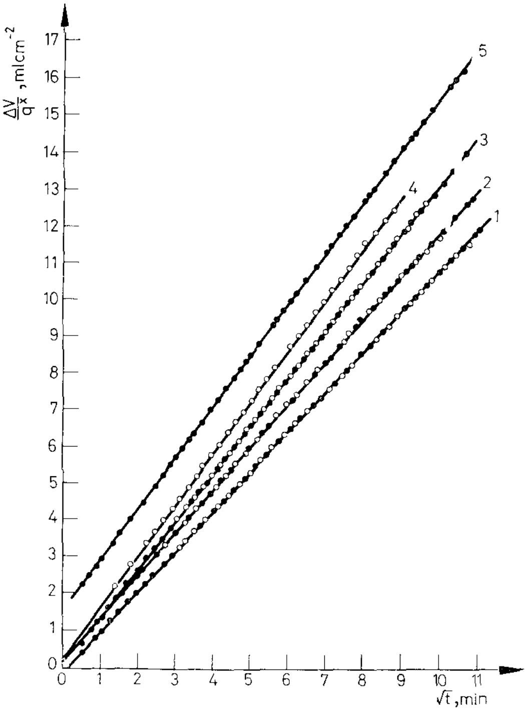

Fig. 4. Oxidation of copper at 1000° at several oxygen pressures, plotted in parabolic system of coordinates. Curves 1—5 correspond to pressures of 5, 10, 20 and 40 mm Hg, respectively. Points — ● — denote the results obtained with the volumetric method, and points — ○ — those with the thermogravimetric method

To test the reproducibility of the results, the measurements were repeated several times under the same conditions of temperature and oxygen pressure, as shown in Fig. 3 by different points. For comparison, in Fig. 4 the results of the present studies are compared with those obtained under the same conditions with the gravimetric method [4]. The values of the parabolic rate constants k_p calculated from the plot are listed in Table 1. The values obtained with the gravimetric method are also given for comparison in this Table. As seen from this comparison and from Figs 3 and 4 the data obtained with the volumetric method show good reproducibility and high precision, and at the same time are in good

Table 1

Parabolic rate constants of copper oxidation
at 1000° for 5, 10, 20 and 40 mm Hg
obtained with volumetric and thermogravimetric methods

Oxygen pressure, mm Hg	No. of measurement	Volumetric method		Thermogravimetric method
		$k_p'' \cdot 10^8$, $g^2\,cm^{-4}\,sec^{-1}$	Relative error, %	$k_p'' \cdot 10^8$, $g^2\,cm^{-4}\,sec^{-1}$
5	1	3.92 ± 0.01	0.25	3.9 ± 0.1
	2	3.92 ± 0.01		
10	1	4.90 ± 0.03	0.61	4.9 ± 0.1
	2	4.95 ± 0.03		
	3	4.91 ± 0.03		
	4	4.91 ± 0.03		
20	1	5.90 ± 0.02	0.34	5.9 ± 0.1
	2	5.91 ± 0.02		
40	1	7.03 ± 0.02	0.28	7.0 ± 0.1
	2	7.01 ± 0.02		

agreement with the results obtained with the gravimetric method. The average absolute error of the values of the parabolic rate constants determined is about 0.02, whereas the analogous error of the gravimetric method amounts to 0.1, in spite of the fact that in these latter studies the microthermobalance applied enabled determination of the mass gains with an accuracy of the order of 10^{-6} g.

Another valuable feature of the method described lies in the simplicity of the measurement, owing to the automatic compensation of the consumed oxygen.

The weak point of the method lies in the relatively small range of oxygen pressures determined by its lower limit. Work on the modification of the apparatus which would allow the extension of the pressure range down to 10^{-4} atm is being carried out at present.

References

1. P. Kofstad, High Temperature Oxidation of Metals, J. Wiley, N. York, 1966.
2. S. Mrowec, Zarys teorii utleniania metali, Wydawnictwo „Śląsk", Katowice, 1971.
3. A. Ciembroniewicz and M. Lasoń, Roczniki Chem., 46 (1972) 703.
4. S. Mrowec and A. Stokłosa, Oxidation of Metals, 3 (1971) 291.
5. C. Wagner and K. Grünewald, Z. Physik. Chem., B. 40 (1938) 455.
6. A. Ronnguis and H. Fischmeister, J. Inst. Metals, 89 (1960 - 61) 65.
7. J. P. Baur, W. D. Bridges and W. M. Fassell, J. Electrochem. Soc. 103 (1953) 273.
8. D. W. Bridges, J. P. Baur and W. M. Fassell, J. Electrochem. Soc., 103 (1956) 475.
9. S. Mrowec and A. Stokłosa, Werkstoffe Korrosion, 21 (1970) 934.

RÉSUMÉ — On décrit un nouvel appareil pour mesurer en continu la cinétique de l'oxydation des métaux aux températures élevées ainsi que pour mesurer l'adsorption et la chimisorption des gaz sur des corps solides. Grâce à sa construction originale, la mesure de la cinétique de la fixation de l'oxygène s'effectue automatiquement avec une très haute précision. On a suivi l'oxydation du cuivre pour définir les caractéristiques de l'appareil.

ZUSAMMENFASSUNG — Eine neue volumetrische Apparatur zur kontinuierlichen Messung der Oxydationskinetik von Metallen bei hohen Temperaturen und zur Messung der Adsorption und Chemisorption von Gasen an Festkörpern wird beschrieben. Eine originelle Konstruktion sorgt für die automatische Durchführung der Messung der Kinetik der Sauerstoffbindung mit sehr hoher Genauigkeit. Die Leistung der Vorrichtung wurde an der Oxydation von Kupfer geprüft.

Резюме — Описан новый волюметрический прибор для непрерывного измерения окисления металлов при высоких температурах и измерения адсорпции и хемисорпции газов на твердых веществах. Благодаря истинному раствору измерение кинетики фиксация кислорода проведено автоматически с очень высокой точностью. С целью испытания прибора было использовано и окисление меди.