

Journal of Nuclear Science and Technology

ISSN: 0022-3131 (Print) 1881-1248 (Online) Journal homepage: https://www.tandfonline.com/loi/tnst20

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To cite this article: Keiji NAITO , Toshihide TSUJI , Tsuneo MATSUI & Katsumi UNE (1974) Purification of Inert Gas, Journal of Nuclear Science and Technology, 11:1, 22-28, DOI: 10.1080/18811248.1974.9730608

To link to this article: https://doi.org/10.1080/18811248.1974.9730608

Published online: 15 Mar 2012.

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Journal of NUCLEAR SCIENCE and TECHNOLOGY, 11[1], p. 22~28 (January 1974).

TECHNICAL REPORT

Purification of Inert Gas

Removal of Oxygen with a Metallic Getter

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Received October 1, 1973

The rate of removal of oxygen from inert gas by metallic getter is measured continuously, and the dilution model is adopted for explaining the rate of purification. The rate of removal of oxygen increases with flow rate. It is found that hydrogen and water vapor present in the inert gas contributes very effectively to reducing the oxygen partial pressure. The rate of removal of oxygen with a titanium getter increases with temperature below about 800°C, but levels off above about 800°C.

***KEYWORDS:* purification, inert gas, oxygen removal, oxygen partial pressure, metallic getter, dilution model, controlled atmosphere, hydrogen water, half period, titanium sponge, temperature dependence, flow rate**

I. INTRODUCTION

There is a rapidly growing need for pure inert gases in various chemical and metallurgical processes as well as in the electronic and nuclear fields. In academic research the use of highly reactive materials of toxic substances such as uranium metal and uranium carbides require a particularly high degree of purity for the inert gases employed[1][2].

The principal contaminants that have to be considered in commercial inert gas are: oxygen, nitrogen and water vapor; less frequently hydrogen, organic vapors or acid vapors have to be removed. Many methods and materials have been used for removing these contaminants[1]. The processes most commonly used for purification of inert gas fall in general into two categories: chemical and physical processes. In the first-named approach, gas-solid chemical reactions such as the use of metallic getters for removing oxygen or nitrogen, and catalytic processes such as the catalytic combination of oxygen and hydrogen over palladized asbestos are practices. The physical processes comprise physical adsorption, refrigeration and low-temperature distillation.

In the first actual preparation of argon by Ramsay in 1894, heated copper was used for removing oxygen and then heated magnesium for removing nitrogen[3]. There have been many studies since then, and a widely used method for eliminating oxygen and nitrogen is that utilizing metal gettering reactions.

Past studies on the purification of inert gas with various metallic getters are summarized in **Table 1**. The efficacy of various metals for the removal of impurities under controlled physical conditions such as particle size, temperature of reaction and gas flow rate have been the main subjects of many past reports. But only limited studies have been based on continuous analysis of the oxygen partial pressure in a flowing system.

In the present paper the oxygen partial pressure in an inert gas purified with metallic getter

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Table 1 Studies on purification of inert gas with various metallic getters

Inert gases	Impurities	Metallic getter	Temperature range (℃)	Method of analysis	References
Inert gases	H_2 O_2, CO_2, N_2, CO, NO *etc.*	U	200～ 250 500～1,000		(4)
Ar	O_2, N_2	Ti	850		(5)
Ar, He	N_2	Ti	900～1,000	Kjeldahl method	(6)
Inert gases	O_2	Cu	550	Mass spectrometer	(7)
Ar	O_2, N_2	Ba, Zn Ca Cu Ti U, *etc.*	200～ 400 600～ 700 200～ 600 600～1,000 175～ 900	Mass spectrometer	(8)
Inert gases	O_2	Cu	550～ 600		(9)
Ar	O_2, H_2O	Al-Mg, K-Na	800～1,000		(10)
Ar	CO, CO_2 O_2 H_2O	U	100～ 930 0～ 740 0～ 800	Infra-red gas analyzer Hersch cell Frost point hydrometer	(11)
Inert gases	O_2, N_2 H_2	Ti Cu Ti	815～ 875 600 205～ 430		(12)
Inert gases	O_2, H_2O, N_2, CO_2, H_2, CO *etc.*	Ca Ti Cr Mn	430～ 705 760～ 815 260～ 370 205～ 260		(13)
Ar	O_2	MnO	150	Hersch cell	(14)
Ar	N_2	Ti	900	Kjeldahl method	(15)
Ar	O_2, N_2	50% Ti-Zr	900	Mass spectrometer	(16)
Inert gases	O_2 N_2 H_2 H_2O	Ti, Ta, Nb, Zr, Hf	700～1,050 800～1,050 350～ 500 700～1,050	Luminous reaction of yellow phosphorus Kjeldahl method Gas chromatograph Dew point meter	(17)

has been measured continuously using nonstoichiometric cobaltous oxide wire. A discussion is given on the effects not only of the temperatue of reaction and gas flow rate, but also of hydrogen and water vapor in the purification of inert gas.

II. Theory

We will first discuss the model representing the purification process of inert gas by metallic getter.

The conditions governing the model are represented schematically in **Fig. 1**. After passing

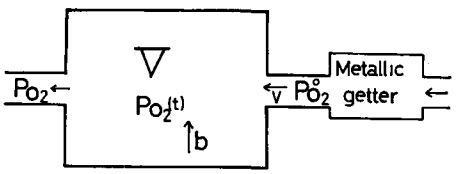


Fig. 1 Dilution model

through the metallic getter, the inert gas containing oxygen at a partial pressure of $P_{O_2}^{\circ}$ atm enters the system of volume V cc at a flow rate of v cc/sec. After passing through the system, the gas leaves it with the oxygen partial pressure modified to P_{O_2} atm. The net change with time of the oxygen partial pressure leaving the system is given by the differential equation

$$dP_{O_2}/dt = \{(P_{O_2}^{\circ} - P_{O_2})v + b\}/V, \quad (1)$$

where b atm cc/sec is the gas leak into the system or the generation of gas in the system. Using the initial condition of the oxygen partial pressure ($P_{O_2}^{in}$, at $t=0$), the solution of Eq. (1) is

$$P_{O_2}(t) = (P_{O_2}^{\circ} + b/v) + (P_{O_2}^{in} - P_{O_2}^{\circ} - b/v) \cdot \exp(-vt/V), \quad (2)$$

where $P_{O_2}(t)$ is the oxygen partial pressure at time t.

This model can be termed a 'dilution model', considering that the concentration of the oxygen in the vessel V is diluted gradually with pure inert gas.

1. Oxygen Partial Pressure at Steady State

When $t=\infty$, Eq. (2) becomes

$$P_{O_2}(\infty) = P_{O_2}^{\circ} + b/v. \quad (3)$$

If a plot of $P_{O_2}(\infty)$ is made against $1/v$, a straight line should be obtained. Using Eq. (3) the oxygen partial pressure $P_{O_2}^{\circ}$ in the inert gas and the amount gas leak or gas generation can be determined from the oxygen partial pressure at steady state under various flow rates.

2. Time Dependence of Oxygen Partial Pressure

Using Eqs. (2) and (3), it is seen that

$$P_{O_2}(t) - P_{O_2}(\infty) = \{P_{O_2}^{in} - P_{O_2}(\infty)\}\exp(-vt/V). \quad (4)$$

Thus, if a plot is made of $\log\{P_{O_2}(t) - P_{O_2}(\infty)\}$ against t, a straight line should be obtained. The slope of this line will be equal to $(-1/2.303)(v/V)$.

Equation (4) is analogous to the equation of radioactive decay: What corresponds to the half-period, τ, is defined by

$$P_{O_2}(\tau) - P_{O_2}(\infty) \equiv (1/2)\{P_{O_2}^{in} - P_{O_2}(\infty)\}, \quad (5)$$

so that $\tau = (\ln 2)(V/v) = 0.693/(v/V)$. (6)

In the case of $b=0$ and $P_{O_2}^{in} \gg P_{O_2}$, Eq. (2) becomes

$$P_{O_2}(t) - P_{O_2}^{\circ} = P_{O_2}^{in}\exp(-vt/V). \quad (7)$$

In the initial period where $P_{O_2}(t) \gg P_{O_2}^{\circ} = P_{O_2}(\infty)$, Eq. (7) is given by the equation

$$P_{O_2}(t) = P_{O_2}^{in}\exp(-vt/V). \quad (8)$$

This equation indicates that the plot of $\log P_{O_2}(t)$ *vs.* t in the initial period should present a linear relation, and that the slope of this line should be equal to $(-1/2.303)(v/V)$. Equation (8) holds when inert gas containing oxygen at very low partial pressure by purification with metallic getter ($P_{O_2}^{in} \gg P_{O_2}^{\circ}$) dilutes the system where there is neither gas leak nor gas generation ($b=0$).

The half-period in this case is the time required for the oxygen partial pressure to decrease to half of the initial value, $P_{O_2}(\tau) \equiv {}^1/_2\, P_{O_2}^{in}$ because $P_{O_2}^{in} \gg P_{O_2}^{\circ}$ and also $P_{O_2}(\tau) \gg P_{O_2}^{\circ}$ in Eq. (5).

Since the half-period is inversely proportional to the slope of the plot of $\log P_{O_2}(t)$ *vs.* t, the smaller the volume of the system (V) and the faster the flow rate (v), the shorter the half-period. Thus, the time required for purification will be shortened by reducing the volume of the system and by raising the flow rate.

III. Experimental

1. Purification of Inert Gas

A diagram of the experimental system is shown in **Fig. 2.** The apparatus is made up of silica and hard glass tubing, and high vacuum grade

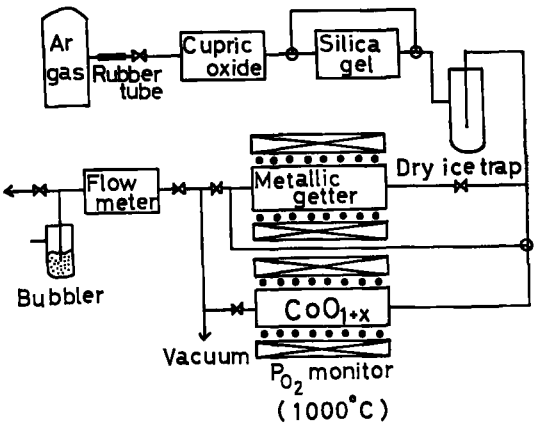


Fig. 2 Experimental system

stopcocks. Gas flow is controlled by a regulator cock and the flow rate measured with a flowmeter.

Hydrogen was removed by heated (370°C) cupric oxide which was prepared by oxidizing copper in air at about 400°C. The gas was then passed through a drying tower containing silica gel, and a dry ice methanol trap. After this, the gas passed into a fused silica tube about 15 mm in diameter, filled with about 2 g of titanium powder to a length of about 13 mm. Titanium, as purchased, almost invariably contains hydrogen, which must be removed by heating at 1,000°C in vacuum for a few hours. Prior to the experiment, the entire system shown in Fig. 2 was evacuated, and then filled with argon gas. The partial pressure of oxygen present in the argon gas immediately after its passage through the titanium sponge (P_{O_2}) was below 10^{-20} atm, as confirmed by measurement using ZrO_2-CaO solid electrolyte fuel cell. However, at the beginning, the oxygen partial pressure at the oxygen monitor was about $10^{-4}\sim10^{-6}$ atm. After passing the purified argon gas, the oxygen partial pressure at the oxygen monitor ($P_{O_2}(t)$) was decreased from an initial value ($P_{O_2}^{in}$) to the final value ($P_{O_2}(\infty)$) gradually with time.

The total volume from the titanium sponge bed to the oxygen monitor in this system (V) is estimated to be about 650 cc.

2. Measurement of Oxygen Partial Pressure

The oxygen partial pressure P_{O_2} was determined in the range of $1\sim10^{-12}$ atm. by measuring the electrical resistance of nonstoichiometric cobaltous oxide wire at 1,000°C. The dependence on P_{O_2} of the electrical resistance of CoO_{1+x} at 1,000°C is shown in **Fig. 3**. In the region of relatively higher partial pressures ($P_{O_2}>10^{-5}$ atm.), the relation $R/R_0\propto P_{O_2}^{-1/4}$ (R_0; R at $P_{O_2}=1$ atm.) is well followed by the results obtained by previous workers[18]~[23]. In the low pressure region, however, good agreement is not seen among their results. In the present case, the relation of the first-cited reference[18] was adopted.

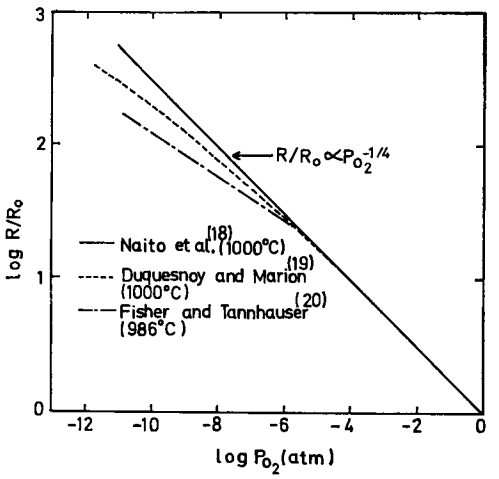
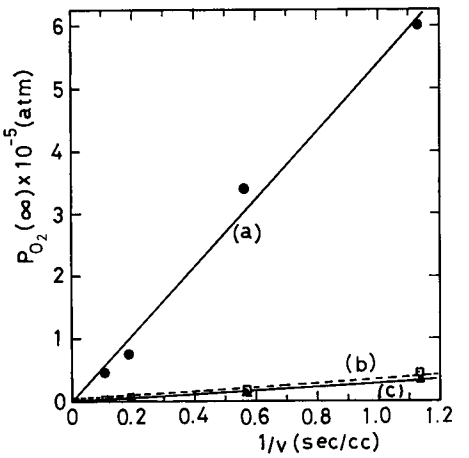


Fig. 3 Dependence of electrical resistance of CoO_{1+x} on partial pressure of oxygen

IV. Results and Discussion

1. Partial Pressure of Oxygen in Argon Gas

Measurements were made of the change in time undergone by the partial pressure of oxygen in argon gas after being fed at constant flow rate through the measuring system without passing through the metallic getter. The partial pressure was found to reach a final steady value ($P_{O_2}(\infty)$). **Figure 4** shows the plot of $P_{O_2}(\infty)$ against $1/v$ for pure and highly pure argon gases. The lines (b) and (c) represent cases where special leaklight rubber tubing specified for use with vacuum was employed in the measuring system, while with use made of ordinary rubber tubing, the corresponding plots gave the line (a). All lines



(a) Highly pure argon (with leaky system)
(b) Pure argon (with very leaklight system)
(c) Highly pure argon (with very leaklight system)

Fig. 4 Plot of $P_{O_2}(\infty)$ against $1/v$ for pure and highly pure argon gases at steady state

indicate a linear relationship between $P_{O_2}(\infty)$ and $1/v$. Using Eq. (3), the value of $P_{O_2}°$, the partial pressure of oxygen in the argon gas entering the measuring system, and b, the rate of gas leak or gas generation, were obtained as shown in **Table 2**.

Table 2 Partial pressure of oxygen in argon gas and gas leak or generation

Argon gas		b(atm. cc/sec)	$P_{O_2}°$ (atm.)
Ordinary pure argon gas	Very leaklight system	3.2×10^{-6}	3×10^{-7}
Highly pure argon gas	Very leaklight system	3.0×10^{-6}	7×10^{-8}
	Leaky system	5.4×10^{-5}	9×10^{-8}

From Fig. 4 and Table 2, it can be recognized that $P_{O_2}°$, is almost the same whether estimated from data obtained from a very leaklight system or from a somewhat leaky measuring system, while the leak rate of the very leaklight system is roughly equal whether for ordinary pure or for highly purified argon gas.

2. Effect of Flow Rate

Figure 5 gives a plot of $\log P_{O_2}(t)$ *vs.* t at 1,000°C under various flow rates. The figure reveals a linear relationship between $\log P_{O_2}(t)$ and t for all flow rates, in accordance with Eq. (8) based on the dilution model, except for the initial period where the system has not yet attained steady state. From the slope of these plots, the half-periods can be determined using Eq. (6). The results thus obtained are plotted in **Fig. 6**, where the theoretical line is also drawn for the case where the geometrical volume (V) of the system is 650 cc. A discrepancy is observed between the half-period obtained experimentally and the corresponding theoretical values. This must be attributed to an increase of the apparent volume (V') that is proportional to the flow rate. Equation (6) is corrected to read

$$\tau' = (\ln 2)\{(V+V')/v\} = (\ln 2)\{(V+vA)/v\} = (\ln 2)\{(V/v)+A\}. \quad (9)$$

The calculated values using Eq. (9) are in good agreement with the experimental values by taking A as 650 sec in this case.

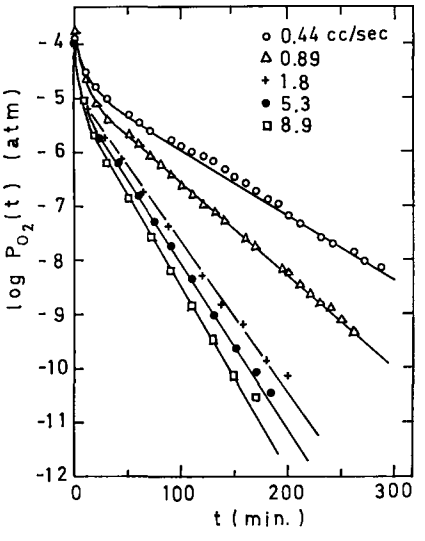


Fig. 5 $\log P_{O_2}(t)$ *vs.* t at 1,000°C under various flow rates

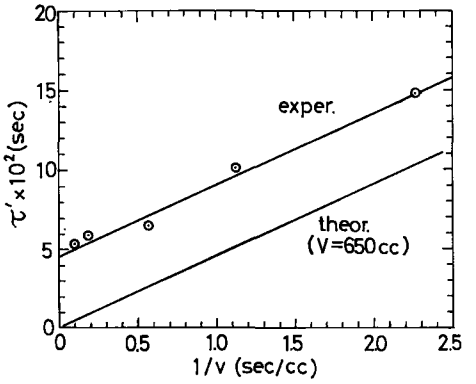


Fig. 6 τ' *vs.* $1/v$ at 1,000°C

The increase observed in apparent volume might be attributed to the generation of oxygen gas absorbed in the system accompanying the increase of the flow rate.

3. Effect of Hydrogen and Water Vapor

The effects of the presence of hydrogen and water vapor upon the rate of oxygen removal were examined for a flow rate of $v=0.89$ cc/sec and at 1,000°C. The results are shown in **Fig. 7**, where the plots marked (a) represent the case where hydrogen was removed by cupric oxide as well as water vapor by dry ice methanol cold trap, while and the plots (b) and (c) correspond to that where only either water vapor or hydrogen was removed, respectively by dry ice trap or cupric oxide.

As seen in Fig. 7, the plots (b) and (c) indicate a behavior quite similar to each other. It is

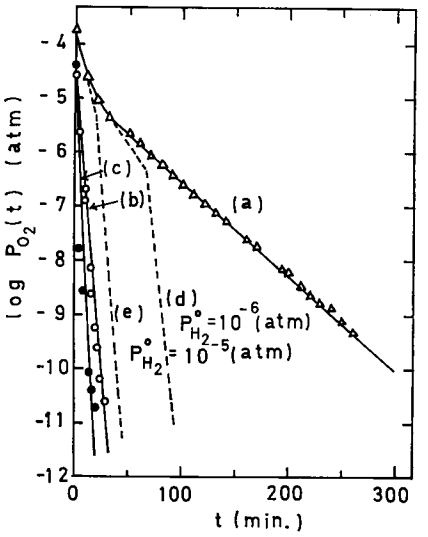


Fig. 7 Effects of hydrogen and water vapors at $v=0.89$ cc/sec and 1,000°C

considered that water vapor reacts with titanium, producing hydrogen by the reaction

$$Ti+H_2O \rightarrow TiO+H_2$$

and that the hydrogen thus produced would react with oxygen:

$$H_2+{}^1/_2\,O_2=H_2O \qquad (10)$$

Letting the initial partial pressures of hydrogen, oxygen and water vapor be represented by $P_{H_2}{}^{\circ}$, $P_{O_2}{}^{\circ}$ and $P_{H_2O}{}^{\circ}$, respectively, the oxygen partial pressure at equilibrium

$$P_{O_2}{}^{e}=P_{O_2}{}^{\circ}-(\alpha/2)\,P_{H_2}{}^{\circ}$$
$$=\{(1/K)(P_{H_2O}{}^{\circ}+\alpha P_{H_2}{}^{\circ})/P_{H_2}{}^{\circ}(1-\alpha)\}^2, \qquad (11)$$

where K is the equilibrium constant of the reaction (10):

$$K=P_{H_2O}/(P_{H_2}\cdot P_{O_2}{}^{1/2}),$$

and α is the degree of reaction of hydrogen with oxygen. In the calculation of $P_{O_2}{}^{e}$, it is assumed that $P_{O_2}{}^{\circ}$ and $P_{H_2O}{}^{\circ}$ are respectively equal to the oxygen partial pressure shown in curve (a) and zero.

The effect of hydrogen partial pressure at 1,000°C calculated from Eq. (11) is shown by dotted lines in Fig. 7, the line (d) being that obtained by assuming $P_{H_2}{}^{\circ}=10^{-6}$ atm., and line (e) that for $P_{H_2}{}^{\circ}=10^{-5}$ atm. The line (e) for $P_{H_2}{}^{\circ}=10^{-5}$ atm. is in fairly good agreement with the observed curves (b) and (c), and also with the analytical values for hydrogen ($P_{H_2}{}^{\circ}<5\times10^{-5}$ atm.), and for water vapor ($P_{H_2O}{}^{\circ}<1\times10^{-5}$ atm.) in the argon gas used.

4. Effect of Temperature

Figure 8 shows the plot of $\log P_{O_2}$ *vs.* t at a flow rate $v=0.89$ cc/sec under various temperatures. It is seen from this figure that the rate of removal of oxygen by titanium getter increases with temperature in the range below 800°C due to increase of oxidation rate by titanium. However, since the time dependence of the oxygen partial pressure at 800°C is almost the same as at 1,000°C, the oxidation rate of titanium above about 800°C is presumably determined by the diffusion of oxygen into the titanium surface.

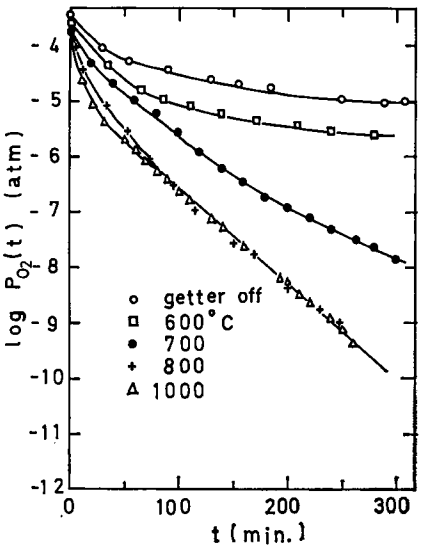


Fig. 8 $\log P_{O_2}$ *vs.* t at $v=0.89$ cc/sec under various temperatures

To summarize, the rate of removal of oxygen increases with flow rate; hydrogen and water vapor present in the inert gas contributes very effectively to reducing the oxygen partial pressure. As an example, using Eq. (8), the time required to reduce the oxygen partial pressure of the system, of a volume of 10^3 l, from that of atmosphere ($P_{O_2}{}^{in}\simeq2\times10^{-1}$ atm.) to $P_{O_2}=10^{-6}$ atm. with a flow rate of 10 l/min is about one day.

REFERENCES

(1) WHITE, P.A.F., SMITH, S.E.: "*Inert Atmospheres*", (1962), Butterworths, London; *Nucl.*

Eng., **7**, 284 (1962).
(2) COOK, G.A.: "*Argon, Helium and the Rare Gases*", Vol. 2, (1961), Intersci. Publ., New York, London.
(3) TRAVERS, W.M.: "*The Discovery of the Rare Gases*", (1928), Edward Arnold.
(4) NEWTON, A.S.: U.S. Pat. 2,521,937, (1950).
(5) MALLETT, M.W.: *Ind. Eng. Chem.*, **42**, 2095 (1950).
(6) DOMBROWSKI, H.S.: *Anal. Chem.*, **26**, 526 (1954).
(7) SHERFEY, J.M.: *Ind. Eng. Chem.*, **46**, 435 (1954).
(8) GIBBS, D.S., SVEC, H.J., HARRINGTON, R.E.: *ibid.*, **48**, 289 (1956).
(9) TOROCHESNIKOV, N.S., BRODYANSKII, V.M., PORTNOI, R.I., *et al.*: *Brit. Chem. Eng.*, **2**, 424 (1957).
(10) PFAFF, W., HOFFMANN, K.: *Arch. Eisenhüttenw.*, **30**, 539 (1959).
(11) DAVIDGE, P.C., HODGE, N., STOCKDALE, G.N.: *Brit. Chem. Eng.*, **5**, 477, 566 (1960).
(12) RENDOS, J.J.: U.S. Pat. 3,061,403, (1962).
(13) OHLGREN, H.A., LEWIS, J.G.: U.S. pat. 3,141,739, (1964).
(14) GEORGE, D.: *AERE-M* 1491, (1965).
(15) KYLE, M.L., PIERCE, R.D., COLEMAN, L.F., *et al.*: *Ind. Eng. Chem. Process Design Develop.*, **7**, 447 (1968).
(16) PACK, J.G., LIBOWITZ, G.G.: *Rev. Sci. Instrum.*, **40**, 414 (1969).
(17) Japan Pure Hydrogen Co. Ltd.: U.K. pat. 1,186,555, (1970).
(18) NAITO, K., KAMEGASHIRA, N., YUTANI, T.: Uupublished work.
(19) DUQUESNOY, A., MARION, F.: *Compt. Rend. Acad. Sci. Paris*, **256**, 2862 (1963).
(20) FISHER, B., TANNHAUSER, D.S.: *J. Chem. Phys.*, **44**, 1663 (1966).
(21) BRANSKY, I., WIMMER, J.M.: *J. Phys. Chem. Solids*, **33**, 801 (1972).
(22) EROR, N.G., WAGNER, J.B.: *ibid.*, **29**, 1597 (1968).
(23) SHELYKH, A.I., ARTEMOV, K.S., SHVARKOUSKII, V.E.: *Sov. Phys. Solids State*, **8**, 706 (1966).
(24) WAHLBECK, P.G., GILLES, P.W.: *J. Amer. Ceram. Soc.*, **49**, 180 (1966).