

# HYDROGEN FUGACITY MEASUREMENTS IN THE SYSTEM Ni-O-H AT ELEVATED TEMPERATURE AND PRESSURE USING Au-Pd MEMBRANE

Rappo O.A. (IEM RAS), Pokrovskii G.S. (LMTG CNRS, Toulouse, France),

Echmaeva E.A. (IEM RAS), Zotov A.V. (IGEM RAS), Osadchii E.G. (IEM RAS)

euo@iem.ac.ru

The hydrogen fugacity was determined in the measuring system, consisting of selective permeable to hydrogen Au<sub>40</sub>Pd<sub>60</sub> membrane, capillaries, valves and a specific absolute pressure detector PX72-030GV (fig. 1).

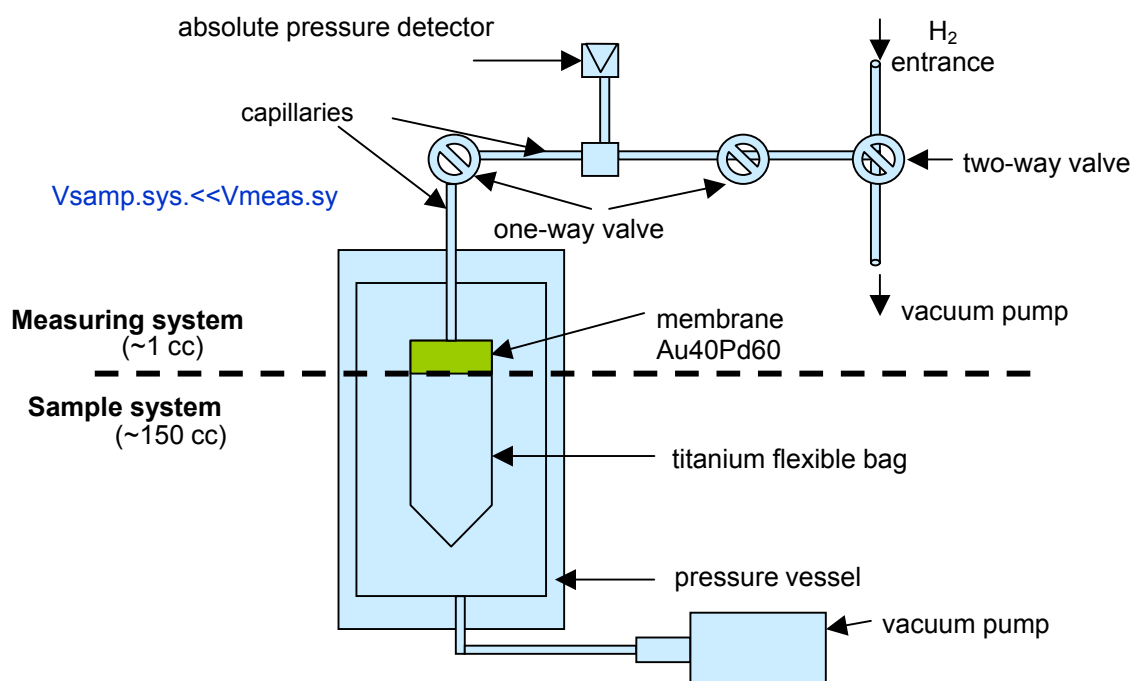


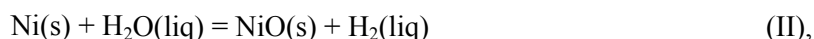
Fig. 1. Principal sketch of the measuring system and CORETEST system

Prior to loading the titanium flexible bag was leak tested by pressuring with N<sub>2</sub>. The measuring system was vacuumised and then hydrogen was flowed inside the measuring system up to atmospheric pressure for 4 times, after each time the vacuumising procedure was repeated. The final result was the system filled with hydrogen at ~1 bar hydrogen pressure in the measuring system. The following reaction was used as a hydrogen generator:



It was realized in the impermeability titanium flexible bag (inner volume ~150 sm<sup>3</sup>), which was connected with measuring system (inner volume <1 sm<sup>3</sup>) by holder with membrane. The flexible reaction bag and pressure vessel were placed in a furnace that rocked through 180 degrees of rotation several times a minute increasing reaction kinetics and homogenizing temperature gradients. The flexible reaction bag contains the fluid and solid reactants for an experiment and is designed to separate these phases chemically and physically from the pressure vessel and the pressure forming medium contained in it.

If the temperature and the total pressure in the reaction bag (sample system) are known, we can define the partial hydrogen pressure in the system using reaction (II)



the GIBBS program and reaction constant ( $K(\text{II}) = f(\text{H}_2)/f(\text{H}_2\text{O})$ ) and the following equation:

$$p(\text{H}_2) = p(\text{tot}) \cdot x(\text{H}_2) \quad (1)$$

where  $x(\text{H}_2)$  is hydrogen mole fraction.

When the system was assembled and placed into the furnace, we started heating the furnace. At  $\sim 418$  K the pressure in the measuring system began to increase gradually and then the temperature was gradually increased to 673 K.

After we achieved stable values of  $E$  at the 673 K temperature and 550 bar pressure (the measuring system was filled with hydrogen), the measuring system was vacuumised to  $\sim 10^{-4}$  bar and we expected the system to achieve steady state. Thus, we check the ability of the system to come to equilibrium at constant  $p$ ,  $T$  parameters. The values of  $E$  (mV) were increasing gradually at the speed of about 2-2.5 mV per 10 minutes at first and then about 0.1 mV per 10 minutes (fig.2). It can depend on the speed of the reaction or the speed of diffusion of  $\text{H}_2$  through the membrane or both. Then we filled the system with hydrogen and made the pressure of  $\text{H}_2$  of  $\sim 1$  bar to check the ability of the system to come to equilibrium at the other side at constant

The measuring system filled with hydrogen

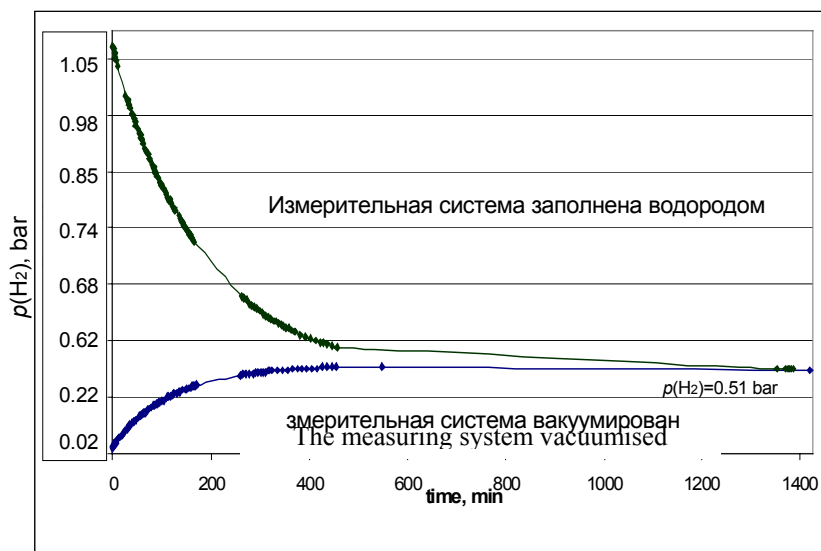


Fig. 2.  $p(\text{H}_2)$ , bar -  $t$ , min dependence

The system came to equilibrium ( $f(\text{H}_2)=0,56$  bar) for 19,2 and 13,3 hours accordingly. The total experiment lasted for 72 hours.

### Calculations

Considering hydrogen fugacity in the investigated system to be equal to hydrogen pressure in the measuring system, the following equilibrium values of  $f(\text{H}_2)$  were determined:  $p_{\text{tot}}=550$  bar,  $f(\text{H}_2)=0,51$  bar (0,58 bar) at  $T=673$  K and  $p_{\text{tot}}=1000$ , bar  $f(\text{H}_2)=0,60$  bar (0,70 bar) at  $T=673$  K. The values in brackets were calculated according to [1] using the GIBBS program (Shvarov, 1991).

$T$ , K	$p(\text{tot})$ , bar	$p(\text{H}_2)$ , bar	$p(\text{H}_2)$ , bar [1]
673	550	0.51	0.58
673	1000	0.60	0.70

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### Reference

1. Kishima N. and Sakai H. Fugacity-concentration relationship of dilute hydrogen in water at elevated temperature and pressure // Earth and Planetary Science Letters, 67. 1984. PP. 79-86.

