Experimental study of metallic mercury solubility in water

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Solubilities of elementary mercury in water in the range of temperatures 120-500^{0}C are devoted the experimental works executed in IEM of the Russian Academy of Sciences [*Sorokin*, 1973; *Sorokin et al.*, 1978; *Sorokin et al.*, 1988]. The great number of publications suffices for an interval 20–120^{0}C along a line of pressure of sated steam of water at a seeming coordination and unity of temperature dependence of solubility are in the obvious contradiction with the reliable high-temperature data (fig. 1).
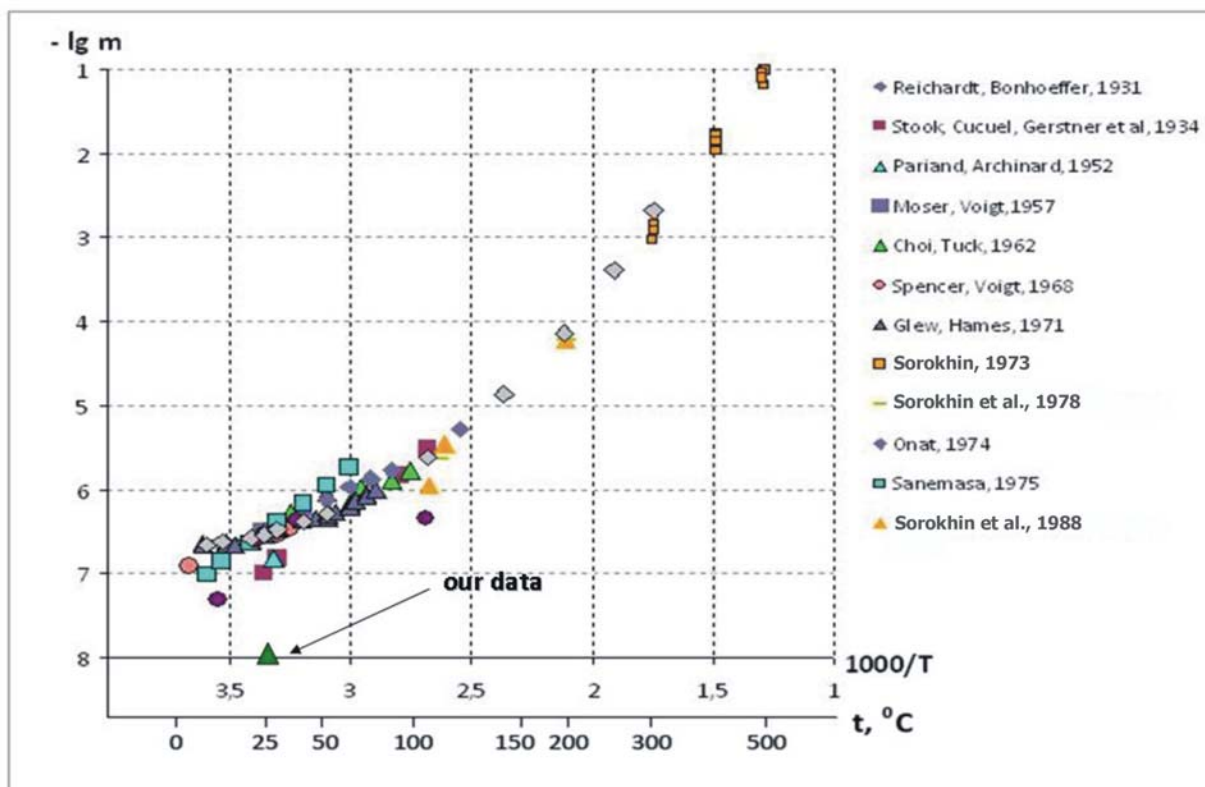

Fig. 1. Solubility of mercury in water as function of inverse temperature

Unusual nonlinearity of dependence lg m – 1/T for simple reaction Hg^0_{liquid} - Hg^0_{aq} at $\Delta C_p = 0$ forces to assume change of the dominating form in a solution in the field of low temperatures. We had been suggested the version about complete dominance of form Hg^0_{aq} (dissolved) at high temperatures when solubility of elementary mercury is high also prevalence of the oxidized forms of mercury at the low.

Extrapolation of this version in area of low temperatures (fig. 2) had been received the value of solubility Hg^0 appropriating at temperature 20^{0}C to concentration 1,99 ppb. Other values of extrapolation are resulted in table 1.

Table 1. The values of concentration calculated on extrapolation of the literary data

t, ^{0}C	1000/T	-lg m	C $_{Hg(0)}$, ppb
20	3,411	8,004	1,99
25	3,354	7,830	2,97
40	3,193	7,343	9,10
60	3,002	6,763	34,65
80	2,831	6,248	113,45
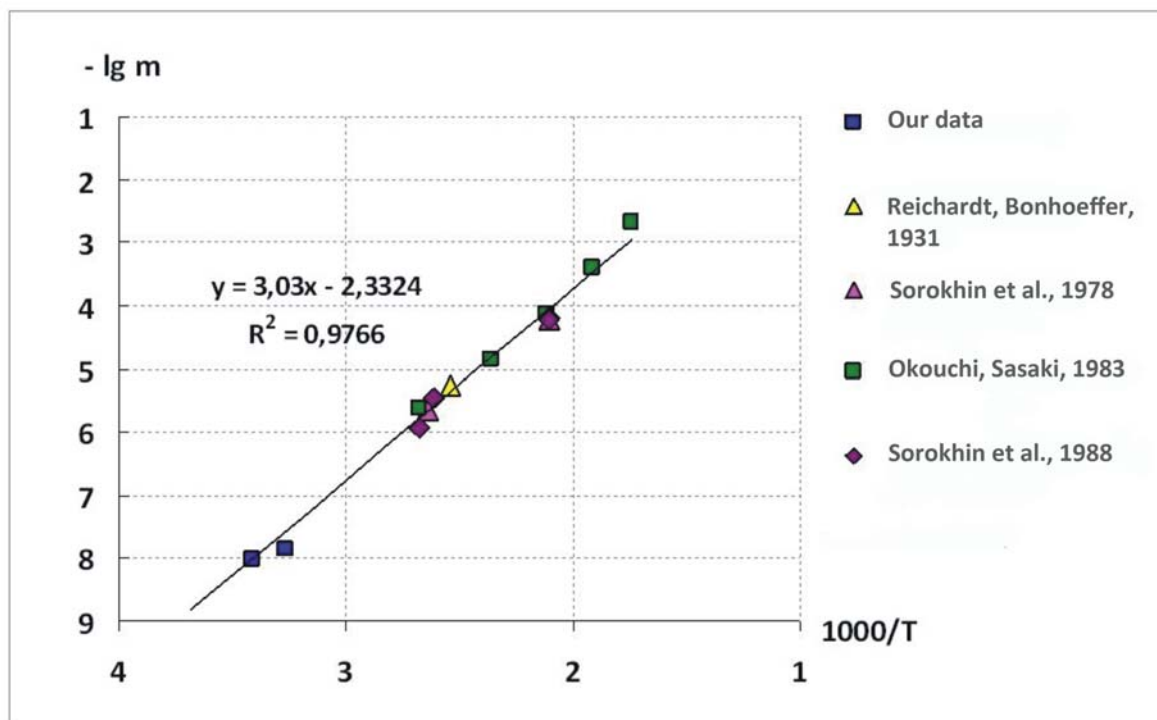
Fig. 2. Extrapolation of the high-temperature data in area of low temperatures and position of our data

During experiment a small amount of metal mercury has been placed in three round-bottomed three-litre flasks with 2,5 litres of twice distilled water. Gases barbotage and sampling were carried out through glass tubes of different length in apertures of bottlenecks. Bottlenecks and all joints have been hermetically sealed by a parafilm. The first flask is left equilibrium with atmospheric air, through two others under pressure argon throughout 15 minutes was passed. In the third flask has initially been added sodium borohydride as a reducer. Scheme of experiment is presented in figure 3.

Samples in volume of 25 ml were selected during experiment some times by means of a 50 ml syringe. At first experience was spent at 20^{0}C. Then the flask №3 has been placed in drying box and sated at temperature 33^{0}C. Under this data kinetic series have been constructed (fig. 4, 5).
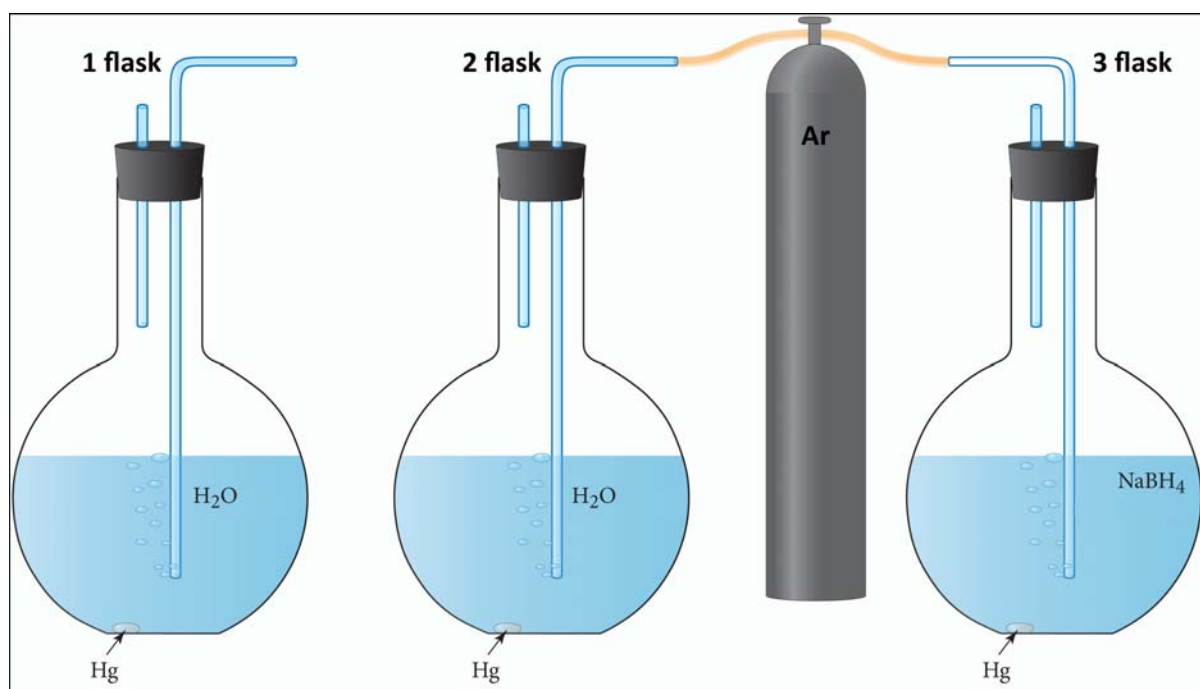
Fig. 3. Scheme of experiment:
1st flask: oxygen atmosphere;
2nd flask: argon atmosphere;
3rd flask: argon atmosphere + $NaBH_4$

Mercury definition on atomic absorber UCM-1MC was spent by a method of cold steam by means of analytical block PAR-3M. The analysis principle is based on discrete measurement of concentration of steams of elementary mercury with preliminary accumulation of this mercury on a collector presented by a double helix sorbent with a gold covering. Mercury collects on a gold substrate, forming an amalgam after that annealing and arrives on the detector which represents atomic absorption photometer with stabilised nonelectrode mercury lamp, length of a wave of radiation: 254 nanometers. Thus, the device registers the contents of elementary mercury. In the beginning samples were put directly, without any preparation, so such way defined quantity null-valent mercury. In parallel aliquots of samples solutions $NaBH_4$ that restored all other forms to null valency before definition of total contents of mercury were brought.
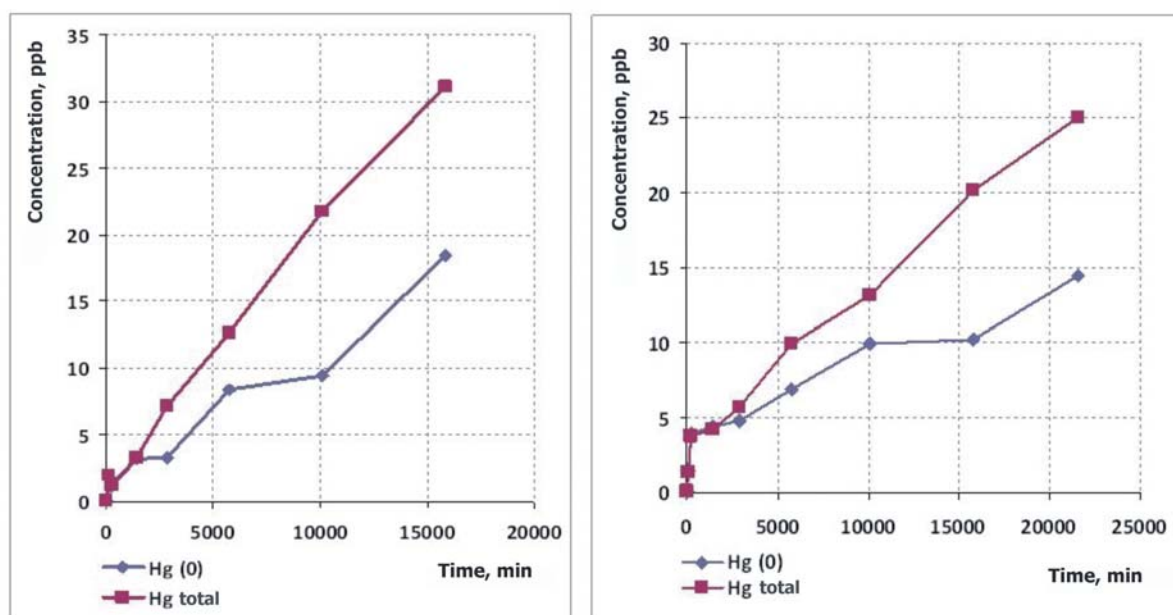

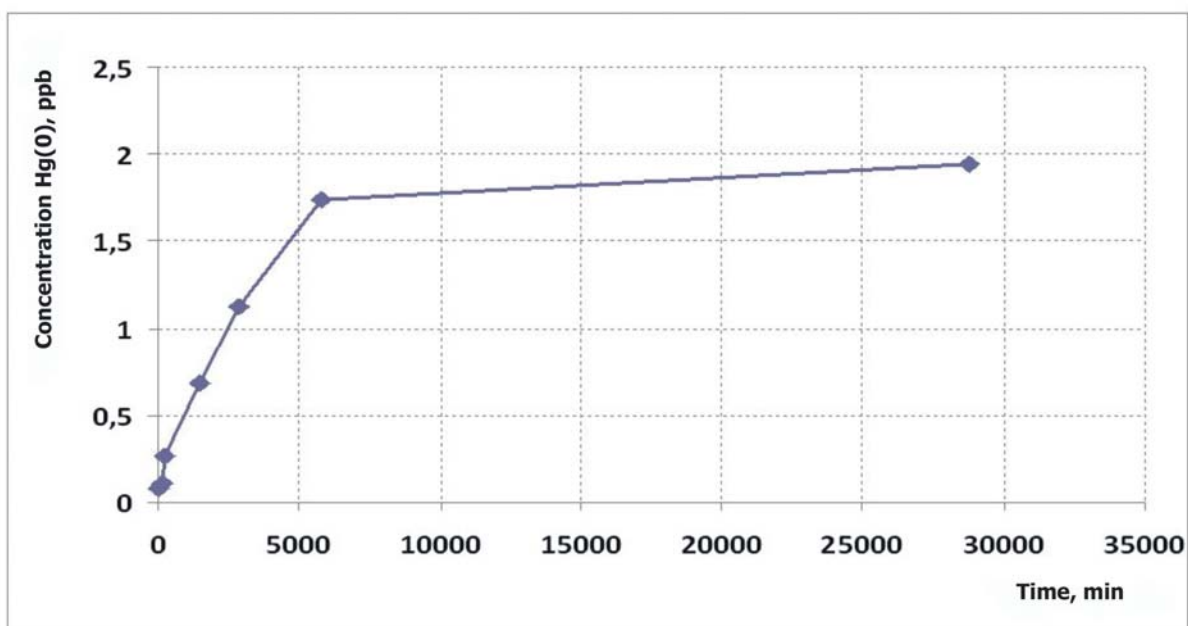**Fig. 4.** Kinetic series at 20 ^{0}C at oxygen and argon atmospheres

Fig. 5. The kinetic series in strongly reducing conditions at 20^0C, which is formed by hydrogen generation on reaction $NaBH_4 + 4H_2O \xleftarrow{\quad\rightarrow} H_3BO_3 + NaOH + 4H_2 \uparrow$

At 33^0C in a flask with oxygen atmosphere has been brought sodium borohydride and, apparently on fig. 6, null-valent mercury concentration in it has fallen and was stabilised in value of 2,75 ppb.
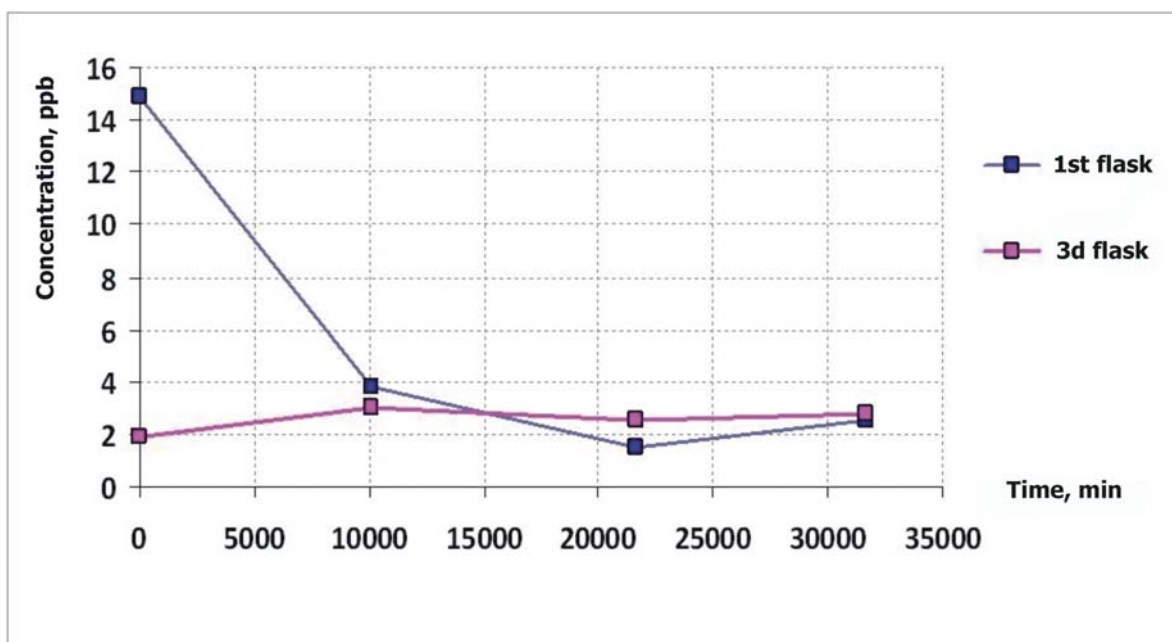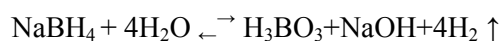

Fig. 6. The approach to balance "from below" and "from above" at $33\ ^0$C in reducing conditions

Intensive reduction realised at the expense of hydrogen, which evidently formed during decomposition reaction sodium borohydride $NaBH_4$ in water:

$$NaBH_4 + 4H_2O \xleftarrow{\quad\rightarrow} H_3BO_3 + NaOH + 4H_2 \uparrow$$

$$NaBH_4 + 2NaOH + H_2O \xleftarrow{\quad\rightarrow} Na_3BO_3 + 4H_2 \uparrow$$

Position of mercury in a standard electrochemical voltage range of metals isn't an obstacle for occurrence of analytically significant concentration of the oxidized forms against the lowest solubility

Hg^0_{aq} at small volatility of steams Hg^0_{liquid} in the field of low temperatures. The made experiments on solubility of mercury in the range of low temperatures in various oxidation-reduction conditions have confirmed this assumption. It is proved by almost absolute coincidence of our data on solubility of mercury in reduction conditions with extrapolated on 20^0 C data in paper [*Sorokin et al.,* 1988]. Linear extrapolation from area of high temperatures for Hg^0_{aq} gives quantity of solubility 1,99 ppb. We experimentally receive value 1,95 ppb. This value on one and a half order more low, than total solubility in oxidising conditions.

Conclusions:
1.Version about domination of form Hg^0_{aq} is experimentally confirmed at high temperatures and the constant of reaction $Hg^0_{liq} - Hg^0_{aq}$ (lg K = lg m = - 8,01) is found at full prevalence of the oxidised forms of mercury in the field of low temperatures, that allows to calculate Henry's coefficients for steams of mercury from the data on fugacity.

2.The quantity of the oxidised forms of mercury in time continuously grows in oxygen atmosphere that speaks about constant oxidation of mercury by water.

3.Values of solubility of 1,95 ppb are experimentally received at 20^0 C that on one and a half order more low, than total solubility in oxidising conditions, and 2,75 ppb at 33^0 C.

Rreferences

Choi, S. S., D. G. Tuck (1962). A neutron-activation study of the solubility of mercury in water. *J. Chem. Soc.* N 797, pp. 4080-4088.

Clever, H. L. (1987). *Mercury in liquids, compressed gases, molten salts, and other elements.* Pergamon Press, 245 p.

Glew, D .N., D. A. Hames (1971). Aqueous nonelectrolyte solutions. Mercury solubility in water. *Canad. J. Chem.* Vol. 49, N 19, pp. 3114-3118.

Kuntz, R. R., G. J. Mains (1964). The solubility of mercury in hydrocarbons. *J. Phys. Chem.* Vol. 68, N 2, pp. 408-410.

Moser, H. C., A. F. Voight (1957). Dismutation of mercurous dimer in dilute solutions. *J. Amer. Chem. Soc.* Vol. 79, N 8, pp. 1837-1841.

Okouchi, S., S. Sasaki (1983). Chemical and Physical behavior of mercury in water. *Rept. Colll. Eng. Hosei Univ.* N 22, pp. 57-106.

Onat, E. (1974). Solubility studies of metallic mercury in pure water at various temperatures. *J. Inorg. Nucl. Chem.* Vol. 36, N 9, pp. 2029-2032.

Pariand, J. C., P. Archinard (1952). Sur la solubilite des metaux dans lean. *Bull. Soc. Chim. France.* F. 5/6, pp. 454-456.

Reichardt, H., K. F. Bohoeffer (1931). Uber das Absorptionsspectrum von gelostem Quecksilber. *Ztsch. Phys.* Bd. 67. H. 11/12, ss. 780-789.

Sorokhin, V. I. (1973). Solubility of mercury in water in the range of temperatures 300-500 ^{0}C and pressure 500–1000 atm. *Doklady AS USSR.* V. 213, №4, pp. 852-855 (in Russ.).

Sorokhin, V. I, Yu. V.Alekhin, T. P. Dadze (1978). Solubility of mercury in systems $Hg-H_2O$, HgS - (Cl)-H_2O and forms of its existence in sulphide forming thermal waters of Kamchatka and island Kunashir. *Sketches physical and chemical petrology.* Issue. 8, pp. 133-149 (in Russ.).

Sorokhin, V. I, V. A. Pokrovsky, T. P. Dadze (1988). *Physical and chemical conditions of formation surmjano-mercury mineralization.* 144 p. (in Russ.).

Stook, A., F. Cucuel, F. Gerstner et al. (1934). Uber Verdampfung, Loslichkeit und Oxidation des metallischen Quecksilber. *Ztschr. Anorg. Und allg. Chem.* Bd. 217. H.3, s. 241.