SOLUBILITY OF OXYGEN AND CARBON DIOXIDE IN WATER

V. I. Baranenko, L. N. Fal'kovskii,
V. S. Kirov, L. N. Kurnyk,
A. N. Musienko, and A. I. Piontkovskii

UDC 621.039.57

Oxygen (O_2) and carbon dioxide enter reactor loops together with water (first filling, makeup water, and water sucked into the turbine condensers). Anionite filters also contribute CO_2 to the water of a reactor loop, even when the anionite is thoroughly prepared beforehand [1].

Table 1 gives the intervals of parameters for which experimental data on the solubility of O_2 and CO_2 in water exist. The experimental data presented have a disconnected and unsystematized character. There are no working expressions for determining the concentration of O_2 and CO_2 at high pressures and temperatures.

The purpose of this paper is to calculate and construct tables of the solubility of oxygen and carbon dioxide in the working regimes of a nuclear reactor. We employed existing experimental data and a method, which we developed [13], in which the limiting concentration of the gas dissolved in the water is described by a relation of the form

$$C_{\text{м}}^{\text{c}} = \frac{P_{\text{vg}} - P_{\text{v}}}{0{,}804 \cdot 10^{-3} K_p K_T P_{\text{in}}}, \text{ cm}^3/\text{g} \qquad (1)$$

where P_{vg} is the pressure of the vapor-gas mixture, MPa; P_v is the partial pressure of the vapor, MPa; P_{in} is the computed internal pressure in the solvent (water), MPa; the coefficient $0.804 \cdot 10^{-3}$ is the factor for converting the concentration from the volume of gas (scaled to normal conditions) into molar fractions; and K_p and K_T are empirical factors that take into account the effect of the pressure and temperature on the solubility of the gas in the water, respectively, determined according to the pressure of the vapor-gas mixture.

To determine the solubility of oxygen and carbon dioxide in water we calculated, based on the existing data [2-12], the values of the coefficients K_p and K_T for O_2 and CO_2. Starting from the assumption that their dependence on the pressure and temperature is nearly linear we performed interpolation and an insignificant extrapolation into the region for which there are no experimental data.

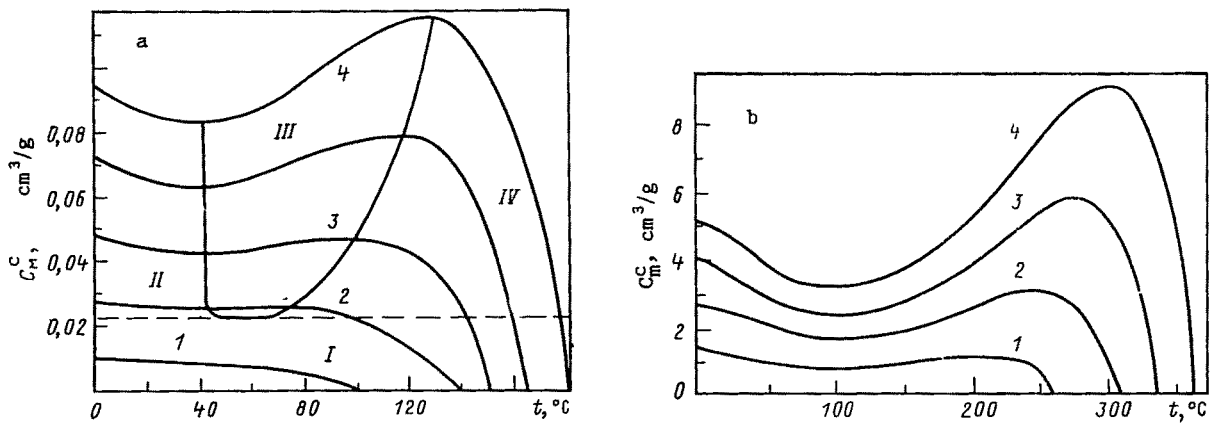

Fig. 1. Isobars of the solubility of oxygen in water at the following pressures (MPa): a) 5 (1), 10 (2), 15 (3), 20 (4), b) 0.1 (1), 0.3 (2), 0.5 (3), 1.0 (4).

Translated from Atomnaya Énergiya, Vol. 68, No. 4, pp. 291-294, April, 1990. Original article submitted October 4, 1988.

 0038-531X/90/6804-0342$12.50

TABLE 1. Ranges of the Parameters of the Solubility of Oxygen and Carbon Dioxide in Water

Dissolved gas	Pressure interval, MPa	Temp. interval, K	Error, meas., %	Reference
Oxygen	0,7—3,5	436—717	1—55	[2]
	0,98—2,6	298	3—5	[3]
	0,67—13,3	305—547	3—5	[4]
	0,7—13,3	298—717	—	[5]
Carbon dioxide	0,1—16,7	273—373	—	[6]
	2,45—49	313—373	—	[7]
	2,45—68,7	323—373	—	[8]
	0,49—15,9	387—621	—	[9]
	1,97—5,8	450—607	—	[10]
	10—50	473—603	—	[11]
	0,1—93	273—373	4	[12]

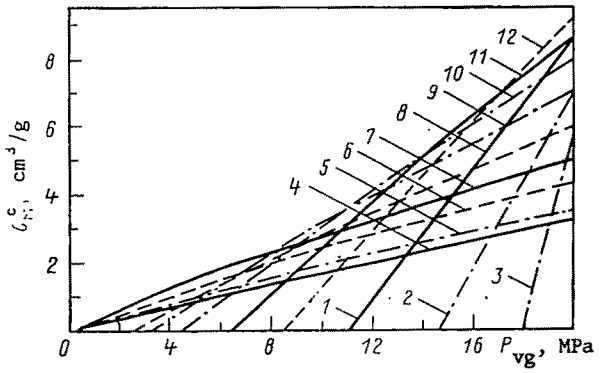

Fig. 2. Isotherms of the solubility of oxygen in water at 320 (1), 340 (2), 350 (3), 100 (4), 60 (5), 40 (6), 0 (7), 220 (8), 240 (9), 260 (10), 280 (11) and 300°C (12).

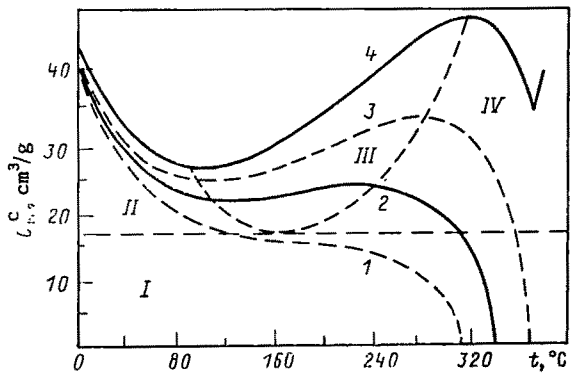

Fig. 3. Isobars of the solubility of carbon dioxide in water at 10 (1), 15 (2), 20 (3), and 25 MPa (4).

TABLE 2. Solubility of Oxygen in Water at High Pressures and Temperatures C_m^c, cm^3/g

P, MPa	Temperature, °C (K)									
	0 (273)	20 (293)	40 (313)	60 (333)	80 (353)	100 (373)	120 (393)	140 (413)	160 (433)	180 (453)
0,1	0,0481	0,0300	0,0207	0,0156	0,0094	0,000				
0,5	0,171	0,146	0,112	0,0941	0,0810	0,0694	0,0554	0,0279		
1,0	0,325	0,285	0,227	0,193	0,171	0,157	0,147	0,128	0,375	
2,5	0,759	0,700	0,573	0,492	0,441	0,422	0,419	0,426	0,427	0,378
5,0	1,456	1,347	1,138	0,964	0,878	0,844	0,868	0,913	0,967	0,996
7,5	2,126	1,971	1,698	1,435	1,295	1,240	1,307	1,374	1,497	1,621
10,0	2,787	2,585	2,249	1,898	1,711	1,641	1,727	1,832	2,013	2,208
12,5	3,416	3,210	2,787	2,347	2,118	2,028	2,130	2,227	2,525	2,786
15,0	4,047	3,809	3,320	2,793	2,522	2,449	2,536	2,717	3,035	3,357
17,5	4,637	4,375	3,834	3,220	2,909	2,778	2,923	3,134	3,493	3,891
20,0	5,193	4,913	4,329	3,630	3,267	3,129	3,292	3,531	3,925	4,397

P, MPa	Temperature, °C (K)									
	200 (473)	220 (493)	240 (513)	260 (533)	280 (553)	300 (573)	320 (593)	340 (613)	350 (623)	360 (633)
0,1										
0,5										
1,0										
2,5	0,293	0,070								
5,0	1,050	1,019	0,776	0,181						
7,5	1,788	1,922	1,872	1,615	0,760					
10,0	2,505	2,808	3,029	2,998	2,504	1,248				
12,5	3,183	3,655	4,084	4,334	4,221	3,350	1,331			
15,0	3,859	4,477	5,103	5,621	5,911	5,354	3,923	0,594		
17,5	4,500	5,263	6,064	6,888	7,295	7,245	6,348	4,058	1,665	
20,0	5,104	6,011	7,064	7,919	8,542	8,958	8,544	7,071	5,665	2,971

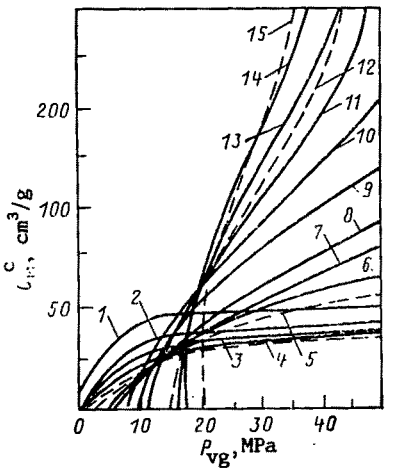

Fig. 4. Isotherms of the solubility of carbon dioxide in water at 0 (1), 20 (2), 40 (3), 60 (4), 200 (5), 220 (6), 240 (7), 260 (8), 280 (9), 300 (10), 320 (11), 340 (12), 350 (13), 360 (14), and 370°C (15).

From the values of K_p and K_T determined in this manner for O_2 and CO_2 we calculated from the formula (1) the limiting concentration of oxygen dissolved in water at pressures up to 20 MPa and temperatures up to 633 K and carbon dioxide at pressures up to 50 MPa and temperatures up to 653 K. The results are presented in Tables 2 and 3. Graphs of $C_m^c = f(P_{vg})$ at T = const (Figs. 1 and 3) and $C_m^c = f(t)$ at P_{vg} = const (Figs. 2 and 4) were constructed based on them.

TABLE 3. Solubility of Carbon Dioxide in Water at High Pressures and Temperature C_m^c, cm^3/g

P_{vg}, MPa	Temperature, °C (K)																					
	0 (273)	20 (293)	40 (313)	60 (333)	80 (353)	100 (373)	120 (393)	140 (413)	160 (433)	180 (453)	200 (473)	220 (493)	240 (513)	260 (533)	280 (553)	300 (573)	320 (593)	340 (613)	350 (623)	360 (633)	370 (643)	380 (653)
0,1	1,789	0,854	0,506	0,298	0,154	0,000																
0,5	8,357	4,322	2,652	1,731	1,304	1,084	0,770	0,352														
1,0	15,36	8,435	5,212	3,406	2,683	2,376	1,980	1,558	0,926	0,000												
2,5	30,85	19,24	11,50	8,037	6,516	5,790	2,295	4,816	4,189	3,369	2,177	0,446										
5,0	41,28	30,54	18,50	13,92	11,34	10,00	9,462	9,025	8,302	7,662	6,944	5,843	4,015	0,841								
7,5	43,19	32,19	22,23	17,64	14,59	12,97	12,32	12,00	11,66	11,24	10,66	9,859	8,745	6,638	2,927							
10,0	44,09	33,08	26,84	22,58	19,31	17,31	16,34	16,34	16,28	16,17	16,06	15,04	14,27	12,67	9,832	4,623						
12,5	44,88	33,79	27,65	24,09	21,13	19,57	18,70	18,71	18,86	18,85	19,00	18,85	18,54	17,63	15,98	12,03	4,700					
15,0	45,40	34,29	28,72	25,17	23,10	22,24	21,35	21,35	22,79	23,36	24,00	24,69	21,60	23,71	23,01	19,79	13,73	1,936				
20,0	46,60	35,53	29,98	27,20	25,64	25,00	25,70	26,71	27,90	29,27	30,86	32,27	33,85	34,41	35,56	34,22	31,43	25,55	19,39	9,793		
25,0	47,51	36,49	30,78	28,56	27,49	27,05	28,15	29,54	31,45	33,25	36,38	39,20	42,14	44,67	47,55	49,86	50,73	48,75	45,05	42,34	35,36	42,48
30,0	48,30	37,36	31,74	29,50	28,50	28,64	30,92	32,71	34,87	37,33	40,70	44,86	49,23	54,98	61,13	66,50	73,05	77,64	80,52	81,29	83,00	88,61
35,0	49,00	38,23	32,66	30,65	29,57	29,94	31,81	34,19	37,07	40,47	44,65	50,14	55,55	64,28	74,05	83,43	95,60	107,0	114,5	119,9	123,4	137,5
40,0	48,80	39,41	33,71	31,79	30,79	31,04	33,65	37,18	40,03	43,42	48,42	55,53	64,59	74,89	88,62	103,4	120,5	144,0	155,8	183,5	196,5	229,0
45,0	50,68	40,50	34,88	32,98	32,05	32,57	35,08	38,27	41,47	44,47	50,23	60,42	69,55	85,00	106,5	129,0	165,9	226,8	266,2	313,8	375,0	496,3
50,0	51,19	40,88	36,26	34,42	33,45	33,34	35,74	38,65	42,21	46,66	51,89	63,35	77,10	99,06	124,2	163,0	221,1	337,6	445,5	658,6	936,2	1214

The isobars of the solubility of the indicated gases (see Figs. 1 and 3) have four specific regions in which the dependence $(\partial C_M^c/\partial T)_p$ is of different character. In the regions I, II, IV $\left(\frac{\partial C_M^c}{\partial T}\right)_p < 0$ and in the region III $(\partial C_M^c/\partial T)_p > 0$. For oxygen the maximum separating the regions III and IV falls into the interval T ≈ 433-573 K; for carbon dioxide it falls into the interval 473-593 K.

Comparing the computed values of the concentration with the experimental values and the interpolated data shows that the computed values C_m^c are virtually identical to the existing experimental values C_m^e. The arithmetic mean error in the computed values C_m^c, compared with the experimental data of [7, 11], is equal to 1.3% for O_2 and 2.5% for CO_2; the maximum error in the computed values C_m^c, is equal to 2.9% for O_2 and 9.5% for CO_2.

The tables of the limiting solubility of oxygen in water in the pressure range 0.1-20 MPa and the temperature range 273-633 K and carbon dioxide in water in the pressure range 0.1-50 MPa and the temperature range 273-653 K, which cover the operating parameters of modern nuclear reactors, were constructed using the values of the internal pressure in water and the existing experimental data.

LITERATURE CITED

1. L. A. Kul'skii and V. A. Blizovskaya, Water in Nuclear Power Engineering [in Russian], Naukova Dumka, Kiev (1983).
2. H. Pray, C. Schweicker, and B. Minnich, "Solubility of hydrogen, oxygen, nitrogen and helium in water," Ind. Eng. Chem., 44, No. 5, 1146-1151 (1952).
3. K. Flolich, E. Tauch, Y. Hogen, and A. Peer, "Solubilities of gases in liquids of high pressure," ibid., 23, 548-550 (1931).
4. L. Zosse, S. Suciv, and W. Sibbit, "The solubility of oxygen in water," Trans. ASME, 76, No. 1, 69-71 (1954).
5. K. M. Grishchuk, "On the solubility of oxygen in water at high temperatures," Teploénergetika, No. 4, 58-60 (1956).
6. V. B. Kogan et al., Handbook of Solubility (in Three Volumes) [in Russian], Izd. Akad. Nauk SSSR, Moscow (1961-1969), Vols. 1-3. Volume 1, Binary Systems. Book 1, compiled by V. V. Kogan, V. M. Fridman, and V. V. Kafarov (1961), pp. 1-960, and Book 2 (1962), pp. 961-1960.
7. K. Wiebe and V. Gaddy, "The solubility of carbon dioxide in water at various temperatures from 12 to 40°C and pressures to 500 atm. Critical phenomena," J. Am. Chem. Soc., 62, No. 4, 815-817 (1940).
8. T. Barry, Chem. Abstr., 251, 92 (1957).
9. A. Ellis, "The solubility of carbon dioxide in water at high temperature," Am. J. Sci., 257, 217-234 (1959).
10. A. Ellis and R. Golding, "The solubility of carbon dioxide above 100°C in water and sodium chloride and in sodium solutions," ibid., 261, 47-60 (1963).
11. S. D. Malinin, "The system H_2O–CO_2 at high temperatures and pressures," Geokhimiya, No. 3, 2352-2450 (1959).
12. Ya. D. Zel'vinskii, "Solubility of carbon dioxide in water at high temperature," Zh. Khim. Prom., 14, 1250-1257 (1937).
13. V. I. Baranenko and V. S. Kirov, "Solubility of hydrogen in water in a wide range of temperature and pressure," At. Énerg., 66, No. 1, 24-28 (1989).