Ozone News, Nr. 1, 1988

THE AQUEOUS SOLUBILITY OF OZONE - A REVIEW

by

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Aqueous saturation values for ozone are important for a fundamental understanding of transfer rates in the dissolving of ozone from the gaseous phase, among other things. Published solubility values, however, differ considerably and there seems to have been no attempt to evaluate critically the available data and to develop a set of best values. Summaries of ozone solubility values by Hallopeau (1) and Mallevialle (2) have not included attempts to resolve differences in the reported data.

In part the present problem has arisen historically. The first extensive set of values, by Mailfert (3), which seem now to be considerably in error at temperatures less than 20°C and greater than 30°C, were later adopted by the International Critical Tables and thus gained unmerited authority. In addition, the thermodynamically implausible statement by Mailfert that the aqueous solubility of ozone drops to zero at 60°C achieved an unfortunately widespread credence. The solubility is difficult to measure because of rapid decomposition of ozone, but it certainly exists.

Published ozone solubilities have been expressed in three forms:

(1) as Bunsen coefficients, β , where β is defined as the volume of ozone at NTP dissolved per volume of water when the partial pressure of ozone in the gas phase is one standard atmosphere;

(2) as the Henry's Law parameter, H_e for the relation $p = H_e \cdot m$, where p is the ozone gas pressure in atmospheres and m is the aqueous ozone concentration in moles per cm^3;

(3) as the solubility ratio, S, where S is the ratio of the solution concentration of ozone, C_ℓ, to the gas concentration, C_g, both expressed in the same units, i.e., g/L, mol./L, etc. Then

$$S = C_\ell / C_g \qquad (1)$$

The parameter, S, has been chosen for presentation of data in this paper, principally because it is most directly related to the experimental analytical figures. All the parameters are easily connected, however. Thus

$$\beta = (273.2)\, S / T \qquad (2)$$

and

$$H_e = (82.04)\, T / S \qquad (3)$$

Fig. 1 presents solubility ratios for essentially all the relevant measurements of aqueous ozone solubility to be found in the literature. A few early individual values, those of Schöne (4) [S = 0.390 (18°)], Carius (5) [S = 0.640 (2°)] and Ladenburg (6) have been omitted. Most of the results, particularly those of Kawamura (7), Stumm (8) and Matrazov et al (9) agree well with one another. The validity of their data is confirmed also by the less extensive results of Briner and Perrottet (10), Razumovskii and Zaikov (11), Rothmund and Burgstaller (12), Muraki (13), Kilpatrick et al. (14), and the Welsbach Laboratories (15). In constrast, the values of Mailfert (3) and those of Rawson (16) disagree with the finding of other studies and with each other. Moreover, they exhibit aberrant trends with temperature. It appears that these last two sets of results should be disregarded.

The solid line drawn in Figure 1 is the proposed best fit to the data. It conforms to the equation

$$\log_{10} S = -0.25 - 0.013t = 3.302 - 0.013T \qquad (4)$$

The line has been constructed to correspond more closely with the upper bound of the concordant data, especially at the higher temperatures, because most of the likely systematic errors, such as failure to achieve equilibrium saturation or loss of dissolved ozone by decomposition, tend to give results that are too low. The overall precision and range of the data do not justify any more than a linear dependence of log S on t.

Table 1 shows some values of S, and $\underline{H}_e$ at rounded temperatures computed in accordance with equation (4). That the solubility values for O_3 at 20° are about seven times those for O_2 is perhaps well known. That the solubility values for O_3 at 60° are still about two and a half times those for O_2, rather than the zero announced by Mailfert, may be less well appreciated.

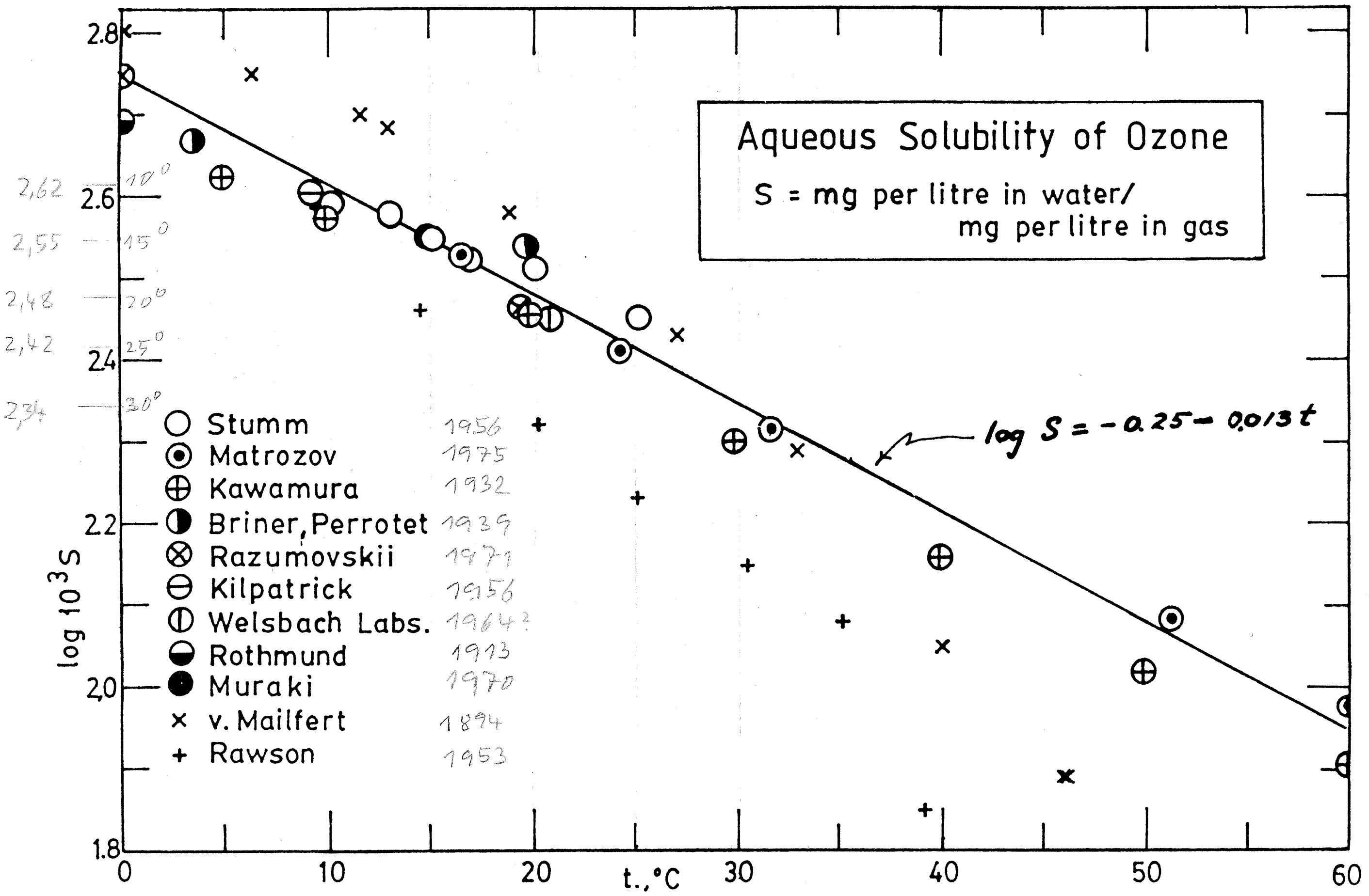

Figure 1. Aqueous Solubility of Ozone as a Function of Temperature.
S = wt O_3 per unit vol. water ÷ wt O_3 per unit vol. in gas phase at one atm. total gas pressure.
Solid line conforms to equation: $\log_{10}S = -0.25 - 0.013\,t$.

$$S = \frac{C_{H_2O}}{C_{Gas}}$$

Table 1

Recommended Values for the Aqueous Solubility of Ozone

Parameter	Temperature, °C										
	0	5	10	15	20	25	30	40	50	60	80
S	.562	.484	.417	.359	.309	.266	.229	.170	.126	.093	.051
β	.562		.402		.288	.244	.206	.153	.107	.076	.039
$10^{-5}\underline{H}_e$	.399		.557		.778	.920	1.09	1.51	2.10	2.94	5.68
1/S	1,78	2,07	2,40	2,79	3,24	3,76	4,36	5,9	7,9	10,7	19,5

Thermodynamically

$$d\ell nS/dT = \Delta E/RT^2 \tag{5}$$

where E is the molar energy of solution. From equation (4)

$$d\ell nS/dT = (2.303)\ (-0.013) = -0.0299 \tag{6}$$

Then, ΔE at 25°C is equal to

$$\Delta E_{298} = -(0.0299)\ (.00831)\ (298.2)^2 = -22.1 \text{ KJ} \tag{7}$$

The enthalpy change, ΔH, for solution is ΔE - RT. So

$$\Delta H_{298} = -22.1 - (.00831)\ (298.2) = -22.1-2.5 = -24.6 \text{ KJ} \tag{8}$$

This is a normal exothermic enthalpy of solution for a non-reactive, slightly soluble gas.

References:

1. Hallopeau, J., "Ozonization". General Report, 6th Congress, International Water Supply Association, Stockholm, Sweden, June 15-19, 1964. pp. D1-D89; English summary pp. D90-D100.
2. Mallevialle, J., in "Ozonization Manual for Water and Wastewater Treatment", W.J. Masschelein, ed. John Wiley and Sons, N.Y. (1982). Chap. 10, pp. 53-56.
3. Mailfert, H., Comptes Rendus 119: 951 (1894)
4. Schöne, Em., Berichte 6, 1224-1229 (1873).
5. Carius, L., Berichte 5, 520-526 (1872); 6: 806-809 (1873).
6. Ladenburg, A., Berichte 31: 2508-2513 (1898).
7. Kawamura, S., J. Chem. Soc. (Japan) 53: 783-787 (1932).
8. Stumm, W., Schweiz. Zeitschrift für Hydrologie 18: 201-207 (1956).
9. Matrozov, V.I., S.A. Kashtanov, A.M. Stepanov and B.A. Trugubov, Zhur, Prikl. Khim 48 (8): 1838-1841 (1975).
10. Briner, E., and E. Perrottet, Helv. Chim. Acta 22: 397-404, (1939).
11. Razumovskii, S.D. and G.E. Zaikov, Isvestia Akad. Nauk. SSSR, Ser. Khim, 4: 689-693 (1971).
12. Rothmund, V. and A. Burgstaller, Nernst Festschrift (1912), pp. 391-394; Monatsh. für Chemie 34: 665-667 (1913).
13. Muraki, V., Suido Kyokai Zasshi 434: 30 (1970).
14. Kilpatrick, M.L., C.C. Herrick and M. Kilpatrick, Journ. Amer. Chem. Soc. 78: 1784-1788 (1956).
15. Welsbach Laboratories, as quoted by J. Hallopeau, ref. 2.
16. Rawson, A.E., Water and Water Eng'g 57, (3): 102-105 (1953).

Comment:

The translation of the concentration of dissolved ozone in water in given experimental conditions into terms of solubility needs several precautions. The data of the literature on the solubility of ozone in water are conflicting particularly when the temperature dependance is concerned. Professor J.C. MORRIS presents here a small overview paper on the topic by analysing on a statistical basis, the thus far published data.

The results of measurement may further depend on the reliability of the analytical methods, and the corrections e.g. for pressure, temperature and the physical properties of the water investigated like ionic strength, pH etc. . . . The comparative analysis of Professor J.C. MORRIS must certainly be an incitation to all IOA-Members to indicate with the necessary details the experimental conditions of their work which could contribute to make further progress on the knowledge of the solubility of ozone in water. Lecturers comments would be greatly appreciated.

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