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COMMMONWEALTH OF AUSTRALIA
Commonwealth Scientific and Industrial Research Organization
Reprinted from: Journal of Physical Chemistry Vol. 67, No. 10, Pages 2233–2235, October 1963

THE IONIZATION OF WATER AT HIGH PRESSURES

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Received April 11, 1963

A large number of measurements have been made of the influence of pressure on the degree of ionization of weak electrolytes dissolved in water,[1] but, rather surprisingly, there have been no direct measurements of the pressure-dependence of the ionization product K_w of water itself at normal temperatures. The main reason lies in the fact that the conductivity methods commonly used in high pressure work are not applicable to water unless it is extremely pure or unless its ionization is greatly enhanced (as it is under the combined

(1) For reviews of the results, see S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths, London, 1957; S. D. Hamann, "Chemical Equilibria: Condensed Systems," in "High Pressure Physics and Chemistry," ed. by R. S. Bradley, Academic Press, London, 1963.

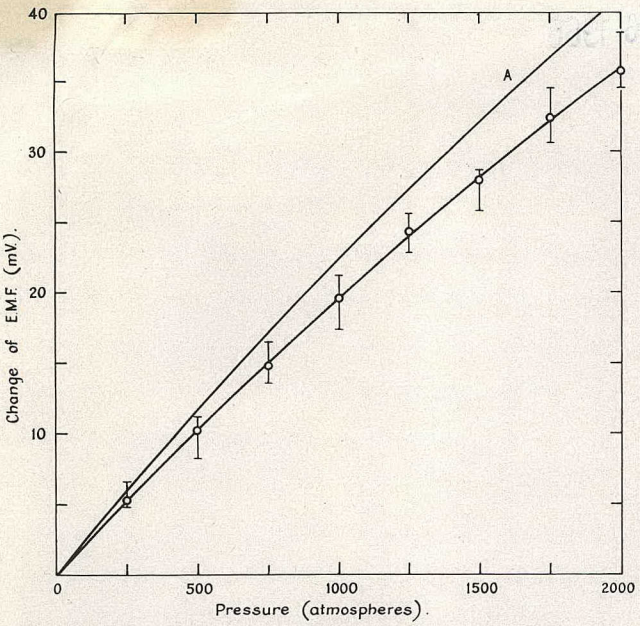


Fig. 1.—The influence of pressure on the e.m.f. of the cell (1) at 25°. It should be noted that the change is actually negative in that it reduces the e.m.f. of the cell. The circles indicate average values derived from measurements on 11 cells; the horizontal lines indicate the *highest* and *lowest* values observed at any particular pressure (the standard deviation is, of course, less than the height of the vertical lines). Curve A is based on Owen and Brinkley's values of $(K_w)_P/(K_w)_1$.

influence of high temperatures and high pressures).[2-4] The problem demands the use of a rather less convenient potentiometric method. Ideally, this should be based on a cell with a hydrogen electrode,[5] but unfortunately there are many practical difficulties in using hydrogen electrodes at high pressures and there is also the serious theoretical problem of properly allowing for the large change of free energy which occurs when gaseous hydrogen is compressed over water.[6] Glass electrodes, although of more dubious thermodynamic standing, suffer from neither of these disadvantages.

Distèche[7-9] has used glass electrodes to measure the effect of pressure on the ionization constants of some weak acids in water and his results agree quite well with those obtained by conductivity methods. In two experiments[9] he obtained evidence that K_w is considerably greater at 1000 atm. than at 1 atm., but the evidence was indirect in the sense that it depended on prior knowledge of the way in which the ionization constants of ammonia and acetic acid change with pressure. The present note describes some rather more direct measurements of K_w based on the use of the cell

Ag	AgCl	aqueous solution of HCl	glass	aqueous solution of KCl + KOH	AgCl	Ag	(1)

in which the molalities of HCl and of KCl were both 0.1 mole/kg. and that of KOH was varied between 0.001 and 0.02 mole/kg. The measurements were made at 25° and at pressures between 1 and 2000 atm. at intervals of 250 atm.

Experimental

The experimental arrangement was similar to the one used by Distèche.[9]

The HCl solution and the Ag|AgCl electrode, constituting the left-hand half of the cell (1), were contained in an open-topped commercial glass electrode made from a rare earth glass which had a negligible alkaline error at pH 13. The right-hand half of the cell comprising the KCl + KOH solution and another AgCl|Ag electrode was held in a surrounding beaker. Pressure was transmitted equally to the two halves by a light hydraulic fluid (dried transformer oil) which surrounded the whole cell and partially filled the glass electrode and beaker.[9]

The Ag|AgCl electrodes were made according to the method of Noyes and Ellis.[10] The potentials of the two electrodes in 0.1 *m* HCl differed by only 0.4 mv., and this difference was found to be unaffected by presssure. The asymmetry potential of the glass membrane was several millivolts and, although it changed slightly with age, in any particular experiment it reached a nearly steady value after one or two pressure cycles and was then independent of the pressure to within 0.5 mv. between 1 and 2000 atm. It was established that the membrane had the correct theoretical response of 59 mv. per pH unit, at 25°, both at atmospheric pressure and at high pressures.

The cell was mounted in a steel pressure vessel of the kind used by Buchanan and Hamann[11] for conductivity work. Electrical leads were taken into the pressure vessel through silica-insulated seals[12] and the complete system of connections, including the oil-insulated leads inside the pressure vessel, had a shunt leakage resistance of not less than 10^{11} ohms. The temperature of the vessel was controlled to within ±0.02° of 25° and the internal pressure to within ±10 atm. of the required value. The e.m.f. of the cell was measured on a Tinsley vernier potentiometer, using a Keithley 610A electrometer as a null-point indicator.

The reagents were of analytical grade and the KOH contained no more than 1% of carbonate.

Results

The following are values of the e.m.f. of the cell (1) measured at the concentrations $m_{HCl} = m_{KCl} = 0.1$ mole/kg. and $m_{KOH} = 0.01$ mole/kg. The results show

Pressure, atm.		1	500	1000	1500	2000
E.m.f., mv.	during compression	631.9	622.1	612.8	604.4	596.6
	during expansion	631.9	622.1	612.1	603.5	

that there was only a slight hysteresis between the compression and expansion phases of the measurements.

Ten other sets of measurements were made on cells in which the concentrations of HCl and KCl were kept the same (0.1 mole/kg.) but that of KOH was varied between 0.001 and 0.02 mole/kg. These cells had, of course, different *absolute* e.m.f. values from those listed above but in every case the *change* of e.m.f. for a particular change of pressure was the same within the reproducibility of the measurements. The mean values of all the results are plotted in Fig. 1.

Discussion

The e.m.f. of the cell (1) is related to the molalities (m) and activity coefficients (γ) of the various ionic species by

$$E = -\frac{RT}{F}\ln K_w + \frac{RT}{F}\ln m_H m_{OH'} + \frac{RT}{F}\ln\frac{\gamma_H\gamma_{Cl}\gamma_{OH'}}{\gamma_{Cl'}} \quad (2)$$

(2) E. U. Franck, *Z. physik. Chem.* (Frankfurt), **8**, 192 (1956).
(3) H. G. David and S. D. Hamann, *Trans. Faraday Soc.*, **55**, 72 (1959).
(4) H. G. David and S. D. Hamann, *ibid.*, **56**, 1043 (1960).
(5) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
(6) W. R. Hainsworth, H. J. Rowley, and D. A. MacInnes, *ibid.*, **46**, 1437 (1924).
(7) A. Distèche, *Rev. Sci. Instr.*, **30**, 474 (1959).
(8) A. Distèche and M. Dubuisson, *Bull. Inst. Oceanogr.* (Monaco), **57**, No. 1174 (1960).
(9) A. Distèche, *J. Electrochem. Soc.*, **109**, 1084 (1962).
(10) A. A. Noyes and J. H. Ellis, *J. Am. Chem. Soc.*, **39**, 2532 (1917).
(11) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).
(12) A. Michels and C. Michels, *Phil. Trans. Roy. Soc.* (London), **A231**, 409 (1933).

where the unprimed quantities refer to the left-hand solutions and the primed quantities to the right-hand solutions. The Debye–Hückel theory suggests that the final term in (2) is unlikely to alter by more than 1 mv. between 1 and 2000 atm. If we ignore this small change,[13] then

$$E_P - E_1 \backsimeq -\frac{RT}{F} \ln (K_w)_P/(K_w)_1$$

where the subscripts P and 1 denote the pressures P atm. and 1 atm. Table I lists values of the ratio $(K_w)_P/(K_w)_1$ derived from the present measurements.

TABLE I

THE INFLUENCE OF PRESSURE ON THE IONIZATION OF WATER AT 25°

Pressure, atm.	$\frac{(K_w)_P}{(K_w)_1}$ (exp.)	$\frac{(K_w)_P}{(K_w)_1}$ (Owen and Brinkley)
1	1.00	1.000
250	1.23	1.261
500	1.49	1.574
750	1.78	1.943
1000	2.14	2.380
1250	2.58	2.893
1500	2.97	3.492
1750	3.53	4.189
2000	4.01	5.000

In 1941, Owen and Brinkley[15] predicted the change of K_w with pressure from the thermodynamic relation

$$\left(\frac{\partial RT \ln K_w}{\partial P}\right)_{T,m} = -\Delta\bar{V}^\infty \qquad (3)$$

where $\Delta\bar{V}^\infty$ denotes the difference between the molar volume of pure water and the partial molar volumes of $H^+ + OH^-$ at infinite dilution. They integrated (3) using the best available data for $\Delta\bar{V}^\infty$ at 1 atm. and for its change with pressure. Their results are shown in Table I and in Fig. 1, where it is apparent that there is a significant discrepancy between the predicted values and those found in this work. It is almost certain that the disagreement arises from a, then, unavoidable error in Owen and Brinkley's calculations. In a recent note Bodanszky and Kauzmann[16] have shown convincingly that the value 23.4 cm.^{3}/mole which Owen and Brinkley took for $-\Delta\bar{V}^\infty$ at 25° and 1 atm. is too large by about 2.1 cm.^{3}/mole.

In this connection it is interesting to examine the pressure dependence of the e.m.f. at atmospheric pressure. Making the justifiable assumption that the ratio γ_{Cl}/γ_{Cl}' is unaltered by pressure, we find that

$$F\frac{\partial E}{\partial P} = -\frac{RT\,\partial \ln K_w}{\partial P} + \frac{RT\,\partial\, \gamma_H\gamma_{OH}'}{\partial P} \qquad (4)$$

$$= \Delta\bar{V}^\infty + (\bar{V}_{OH}' - \bar{V}_{OH}^\infty) + (\bar{V}_H - \bar{V}_H^\infty) \qquad (5)$$

where the terms in parentheses denote the differences between the partial molar volumes of the ions in their actual solutions and at infinite dilution. Since the concentrations of the two solutions were nearly the same (0.1 mole/kg.), the quantity (5) should be close to the change of molar volume $\Delta\bar{V}$ for the hypothetical ionization of pure water into H^+ and OH^- ions, both at the molality $m = 0.1$. Bodanszky and Kauzmann's analysis of density data shows that the volume change for the process

$$H_2O \text{ (pure)} \longrightarrow H^+(m) + OH^-(m)$$

is

$$\Delta\bar{V}/\text{cm.}^3 \text{ mole}^{-1} = -21.28 + 2.57\sqrt{m} - 0.84\, m$$

so that when $m = 0.1$, $\Delta\bar{V} = -20.55$ cm.^{3}/mole. The value of the derivative (4) calculated from the present measurements is -20.4 ± 0.5 cm.^{3}/mole at 1 atm.

To summarize, this note describes the first, nearly direct, measurements of the influence of pressure on K_w. The results disagree with Owen and Brinkley's prediction of the change but confirm Bodanszky and Kauzmann's revised estimate.

Acknowledgment.—The author is indebted to Mr. P. Goldberg for his help in the experimental work.

(13) It should be mentioned that in the present experiments it was impossible to follow the usual procedure of working over a wide range of ionic strengths and extrapolating the results to zero ionic strength to obtain K_w. Glass electrodes only function properly over a rather restricted range of concentrations.[14]

(14) See, *e.g.*, R. G. Bates, in "Reference Electrodes," ed. by D. J. G. Ives and G. J. Janz, Academic Press, New York, N. Y., 1961, p. 258.

(15) B. B. Owen and S. R. Brinkley, *Chem. Rev.*, **29**, 461 (1941).

(16) A. Bodanszky and W. Kauzmann, *J. Phys. Chem.*, **66**, 177 (1962).