고압하에서의 전지의 기전력과 열역학적 성질

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(1974. 7. 8 접수)

The Electromotive Force and Thermodynamic Properties of the Cell at High Pressure

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(Recieved July 8, 1974)

요 약. 종래의 방법으로 고압하에서 전지의 표준기전력($E°$)를 산출하는 것은 불가능하다. 그러나 완전평형상수의 개념을 종래의 Nernst 방정식에 적용하므로서 고압하에서 표준기전력을 구할 수 있게 되었다(완전 Nernst 방정식).

더욱이 다른 열역학적 성질 이를테면 수화수의 순변화(k), 용매의 압축율($β$), 전지반응에서 종래의 해리상수(K) 평형상태에서 표준자유에너지변화($ΔG°$) 표준엔탈피변화($ΔH°$) 및 표준엔트로피변화($S°$) 등을 얻었다.

본 실험에서는 전지의 기전력(E)을 20~35°C와 1~2500 atms 범위에서 측정하였다. 일정한 온도에서 전지의 기전력은 압력이 증가함에 따라 증가하였으며, 일정한 압력에서 온도가 증가함에 따라 역시 증가하였다.

전지반응의 수화수의 순변화(k)는 20°C에서 41.96으로서 압력에 따라 변하지 않고 일정한 값을 유지하였으나 한편 K와 $ΔS°$는 압력에 따라 증가하였으나 $ΔG°$와 $ΔH°$는 감소하였다.

고압하에서도 완전 Nernst 방정식으로부터 표준기전력을 계산할 수 있으므로 상압에서와 마찬가지로 화학평형론을 취급할 수 있게 되었다.

Abstract. It is unable to derive the standard emf($E°$) of the cell at high pressure from the conventional method. However, when the concept of the complete equilibrium constant($K°$) is available to the conventional Nernst equation, it is possible to get the standard emf of the cell at high pressure(complete Nernst equation).

Moreover, the other thermodynamic properties, such as the net change of solvation number(k), the compressibility of solvent($β$) ionization constant(K), the standard free energy change($ΔG°$), the standard enthalpy change($ΔH°$) and the standard entropy change ($ΔS°$) of the cell reaction at equilibrium state have been also obtained.

In this experiment, the emf of the cell; 12.5 % Cd(Hg) | CdSO$_4$(3.105×10^{-3} M), Hg$_2$SO$_4$ | Hg have bee measured at temperature from 20 to 35°C and at pressures from 1 to 2500 atms.

The emf of the cell increased with increasing pressure at constant temperature, and did with in-

creasing temperature at constant pressure.

The net change of solvation number(k) of the cell reaction was 41.96 at 25 °C, and kept constant value with pressure, while, K and ΔS° increased with pressure, but whereas ΔG° and ΔH° decreased.

Since the standard emf of the cell at high pressure can be calculated from the complete Nernst equation, the theory of chemical equilibrium could be developed with at high pressure as well as at the atmosphere.

2. Introduction

Studies of the electromotive force(emf) of the electrochemical cell at high pressure were seldom done until today. G. N. Lewis and M. Randall had measured the emf of the hydrogen electrode with changing the pressure of hydrogen refering to the calomel electrode in 1914.[1~3] But they presumed that the emf of the calomel electrode does not change at all by pressure. E. Cohen and K. Piepenbrock had also measured the emf of the cell;

$$Tl(Hg)\,|\,Tl\,CNS\,(s),\quad KSCN(m)\,\parallel\,KCl\,(m),$$
$$TlCl(s)\,|\,Tl(Hg)$$
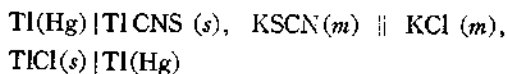
at high pressure and calculated the volume change of the the cell reaction in 1934.[4] Recently, various studies at high pressure have imposed many useful information of geochemistry for evaluating hydrothermal processes and application in oceanography. But the emf of the cell were exceptional part in high pressure, because of its theoretical imperfection on measurement of the standard electromotive force of the electrodes and the difficulties of experiments. As impetus for this renewal of interest in the effect of pressure on the conductivity of the electrolyte solution, W. L. Marshall have studied the complete equilibrium constants of the dissociation reaction of some simple salts by the conductivity method at high pressure and concluded that the complete dissociation constant of the salts is invariable with pressure.[5,9~13] This

simple conclusion have made it enable for us to derive the standard electromotive force of the cell from which various thermodynamic properties are deductable. Up to today, most properties of the solutions are studied from the conductance method at high pressure. This method is not only too complication but also difficult, i.e. the dielelectric constant and viscosity of the solution must be know forehand deriving its thermodynamic properties.[6,8] On the contrary, emf method is quite simple when the standard emf is available.

Complete Equilibrium Constant and Complete Nernst Equation. Complete equilibrium constant for the reaction of the cell; $M\,|\,M^+A^-$ $(m),\ M'A(s)\,|\,M')$

$$M + M'A_{(H_2O)j} + k_{H_2O} \rightleftarrows$$
$$M^+_{(H_2O)m} + M' + A^-_{(H_2O)n} \qquad (1)$$
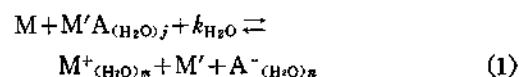
is

$$K^\circ = a M^+_{(H_2O)m}\, a A_{(H_2O)n} / a M'A_{(H_2O)j}\, a^k_{H_2O} \qquad (2)$$

where

$$k = m + n - j \qquad (3)$$

The realation between conventional equilibrium constant(K) and complete equilibrium constant (K°) is

$$K^\circ = K / a_{H_2O}^k \qquad (4)$$

Conventional Nernst equation for the cell in which reaction(1) takes plece is

$$E = E^\circ + \frac{RT}{nF}\,\ln J_a \qquad (5)$$

Where

$$J_a = a\mathrm{M}^+_{(\mathrm{H_2O})m} \, a\mathrm{A}'_{(\mathrm{H_2O})n} / a\mathrm{M}'\mathrm{A}_{(\mathrm{H_2O})j} \quad (6)$$

$$E^\circ = \frac{RT}{nF} \ln K \quad (7)$$

Similary, the complete Nernst equation can be represented as the following;

$$E = E_c^\circ + \frac{RT}{nF} \ln J_a^\circ \quad (8)$$

Where

$$J_c^\circ = a\mathrm{M}^+_{(\mathrm{H_2O})m} \, a\mathrm{A}^-_{(\mathrm{H_2O})n} / a\mathrm{M}'\mathrm{A}_{(\mathrm{H_2O})j} \, a^k_{\mathrm{H_2O}}$$
$$(9)$$

and

$$E_c^\circ = \frac{RT}{nF} \ln K^\circ \quad (10)$$

Standard Electromotive Force and Thermodynamic Properties. Equation(8) can be expanded as the follow;

$$E = E_c^\circ + \frac{RT}{nF} \ln J_a - l \frac{RT}{nF} \ln a_{\mathrm{H_2O}}. \quad (11)$$

Comparison of the two equations (5),　(11) shows that

$$E_c^\circ = E^\circ + k\frac{RT}{nF} \ln a_{\mathrm{H_2O}} \quad (12)$$

which is equivalent to the relation shep of two equilibrium constants

$$K = K^\circ a_{\mathrm{H_2O}}^k.$$

According to equation(12), when the water activity is approaching unity, both standard emf's are the same. At room temprature and atomospheric pressure the activity of water is approarching unity in dilute solution.

This means that the two standard emf' are indifferent at such conditions. Accordingly, complete emf(E_c°) is invariable with pressure change, while conventional standard emf(E°) depends upon pressure. This fact means that complete standard emf can be determined experimentally by measuring the emf of the cell with pressure change.

Differentiation of Eq. (11) with respect to pressure at constant temperature yields the following equation, because E and K are independent of pressure as above mentioned.

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{RT}{nF}\left[\left(\frac{\partial \ln Ja}{\partial P}\right)_T - k\left(\frac{\partial \ln C_{\mathrm{H_2O}}}{\partial P}\right)_T\right]$$
$$(13)$$

Plotting $\left(\dfrac{\partial E}{\partial P}\right)_T vs. \left(\dfrac{\partial \ln C_{\mathrm{H_2O}}}{\partial P}\right)_T,$ we can calculate form its slope. To get the derivatives both E and $(\ln C_{\mathrm{H_2O}})$ should be expressed by the power series of P at constant temperature by using "the method of least square". On the other hand, the mole concentration of water $(C_{\mathrm{H_2O}})$ in the dilute solution can be had from the next equation

$$C = \frac{1000\,d}{M}, \quad (14)$$

where d is the density of water at the given temperature and pressures, and M is the molecular weight of water. In the case of dilute solute solution, the concentration of water can be used instead of the activity of water. Substituting it in eq. that the k value obtained from the slope of eq. conventional equilibrium constant(K) is deductable at arbitrary pressure range. From the conventional equilibrium constant, the conventional standard emf of the cell is deductable at arbitrary pressure.

The standard volume change (ΔV°) of the cell reaction can be derived from the next equation.

$$\left(\frac{\partial E^\circ}{\partial P}\right)_T = -\frac{\Delta V^\circ}{nF} \quad (15)$$

In eq. (15) if E° is expressed in volts, p in atomosphere, ΔV° in cm^3 and F in coulomb, then it becomes[14]

$$\left(\frac{\Delta E^\circ}{\Delta P}\right)_T = -\frac{0.1034\,\Delta V^\circ}{nF}\left(\frac{\mathrm{volt}}{\mathrm{atm}}\right). \quad (16)$$

Taking the natural logarithm of the both sides and replacing the activity coefficient of water by concentration in eq. (4) one obtaines

$$\ln K = \ln K^\circ + k \ln C_{H_2O}. \qquad (17)$$

Substituting eq. (14) into the eq. (17), we have

$$\ln K = \ln K^\circ + k\, 55.51 + k \ln d. \qquad (18)$$

Because both K and are not the function of pressure, diffrentiation of eq. (18) with respect to pressure (P) at constant temperature (T), yields[13]

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = k\left(\frac{\partial \ln d}{\partial P}\right)_T \qquad (19)$$

$$= k\beta \qquad (20)$$

where $\left(\frac{\partial \ln d}{\partial P}\right)_T$ is the compressibility of the solvent (β) using the follwing equation of the thermodynamics know one has from eq.

$$G^\circ = -nFE^\circ = -RT \ln K, \qquad (21)$$

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^\circ}{RT}. \qquad (22)$$

Combining this result with eq. (20), we have

$$\Delta V^\circ = -k RT \beta. \qquad (23)$$

Putting k and ΔV° obtained from eq. (13) and eq. (16) respectively into eq. (23), we have the compressibility of solvent (β),

Accordingly, the emf (E) of the cell in which the same reaction as eq (1) take place, can be measured with increasing pressure at a certain temperature and the conventional standard emf (E) of the cell at each pressure can be calculated.

Incidentally, the above mentioned various thermodyamic properties can be measured. From those grounds, we have made cadmium cell; 12.5% Cd(Hg)/CdSO$_4$(3.105×10^{-3} M), Hg$_2$SO$_4$ (s)/Hg. and measured the cell by changing the pressure from atomospheric pressure to 2,500

atms and temperature frcm 15 to 25 °C. Frcm the data the conventional standard emf (E°) and other thermodynamic properties were culated and also discussed the phenomenal results.

2. Experimental

Materials. Cadmium amalgam(12.5 %) was prepared from the extrapure grade of cadmium metal and refined mercury from the exact weighing. The pure cadmium sulfate and solid mercurous sulfate were reagent grade chemicals.

Electromotive Force Cell. The cell which ιs shown in *Fig* 1. was made of hard glass, about seven centimeters long three centmeters wide. The platinum leads were sealed in at its both ends and a small mercury reservior was fixed to its low parts. The concentration of cadmium sulfate solution was determined by means of the chelate titratration. Mercurous sulfate powder, mercury and cadmium sulfate solution were mixed completely and made into the paste. The other parts of the method to make the cell were in accordance with that of the common Weston cell except the concentration of the solution. The upper stopper of the cell was sealed completely by mercury in order to prevent the oil from infiltrating into the cell.
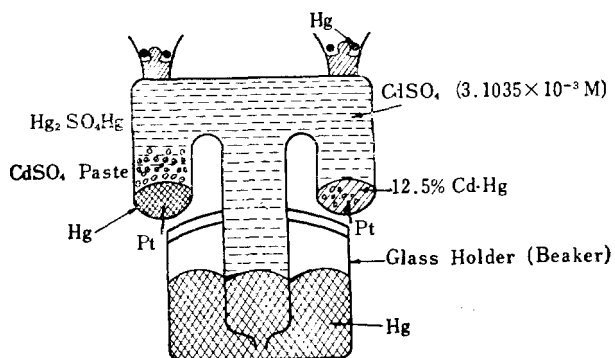

Fig. 1.

Pressure Apparatus and Electromotive Force Measurements. The pressure vessel is show in *Fig.* 2. It is of a kind by E. Whalley[15,16]

and his coworkers and was made of SKD-11 Steel.

The electrical seals were made with mica and neoprene rubber O-rings and were held in place by a Bakelite retaining plate. The resistance between leads and the head was larger than 200 KΩ at all pressures and temperatures. The cell was supported by a stainless steel holder which was suspend from the head of the pressure vessel by wires attached to hooks screwed into the head. A schematic drawing of the essential high-pressure equipment is shown in *Fig* 3. The pressure-transmitting fluid was medium grade spindle oil and pressure was generated by a hand-operated pressure pump(Swiss Nova). The pressure was measured by Heise Bourdon gauge. The thermostat was conteolled to $0.01°C$. The electromotive force was measured by a DC potentio meter

In this experiment the measurements of the emf(E) of the cell were made from 1 to 2500
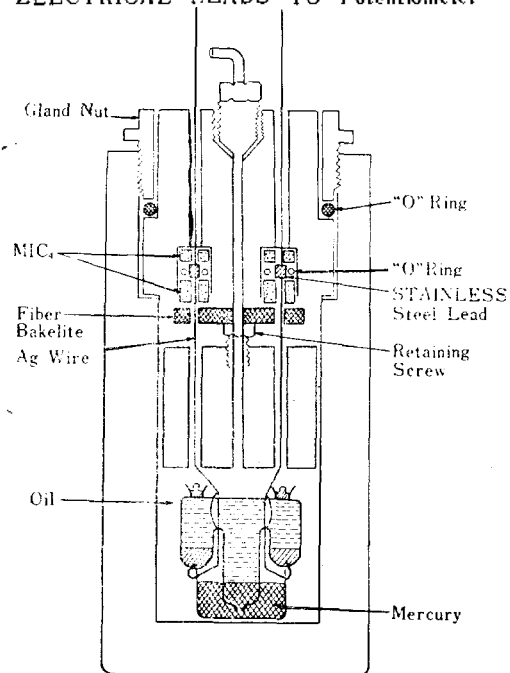
ELECTRICAL LEADS TO Potentiometer


Fig. 2.

atms and from 20 to 35°C.

All measurements were made after elapsing sufficiently long time for the system to attain a new equilibrium after pressure.

3. Results and Discussion

The emf of the cell increases not only with increasing pressure but also with temperature. At constant temperature the change of the emf was large at low pressure range, whereas it was small at high pressure range as in shown in *Fig* 4.

The emf of the cell as function of temperature at constant pressure showed the linear relationships as in the *Fig* 5.
The cell reaction studied, was

$$Cd(Hg) + Hg_2SO_{4(H_2O)j} + k_{H_2O} \rightleftharpoons$$
$$Cd^{+2}_{(H_2O)m} + 2Hg(l) + SO_4^{-2}_{(H_2O)n} \qquad (24)$$
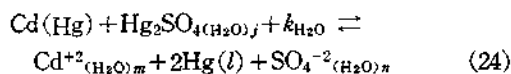
and its emf was denoted by means of the complete Nemst equation as follows;

$$E = E_c° + \frac{RT a_{Cd^{+2}(H_2O)m} a^2_{Hg(l)} a_{SO_4^{-2}(H_2O)n}}{2F \; a_{Cd(Hg)} \; a_{Hg_2SO_4(s) (H_2O)j} a^k_{H_2O}}$$

$$= E_c° + \frac{RT}{2F} \ln Ja° = E_c° + \frac{RT}{2F} Ja/a^k_{H_2O}. \quad (25)$$

Let us consider the emf(E) of the cell increases with increasing pressure and temperature. Supposing that the activities of Hg(l), Cd(Hg), HgSO(s)(HO) are unity, the eq. (25) become

$$E = E_c° + \frac{RT}{2F} \ln \frac{a_{Cd^{+2}(H_2O)m} a_{SO_4^{-2}(H_2O)n}}{a^k_{H_2O}} .$$

Table 1. The emf of the cell at integral tempeatures and pressures

Temp (°C)	Press. (atms)					
	1	500	1000	1500	2000	2500
20	1.1045	1.1129	1.1199	1.1247	1.1283	1.1329
25	1.1060	1.1152	1.1222	1.1270	1.1330	1.1361
30	1.1075	1.1175	1.1245	1.1295	1.1343	1.1382
35	1.1110	1.1201	1.1272	1.1324	1.1362	1.1402
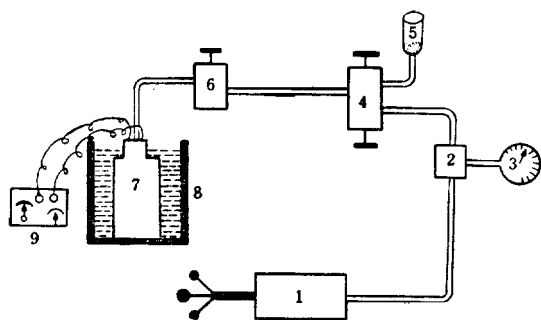
Fig 3. Schematic drawing of equipment for electro-
motiveforce measurements at high pressures.

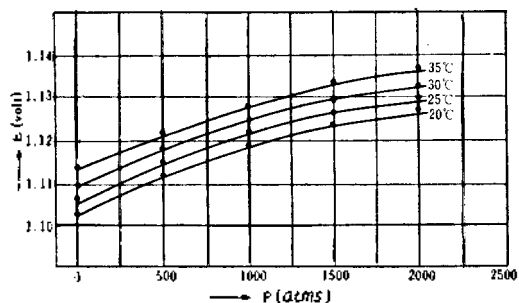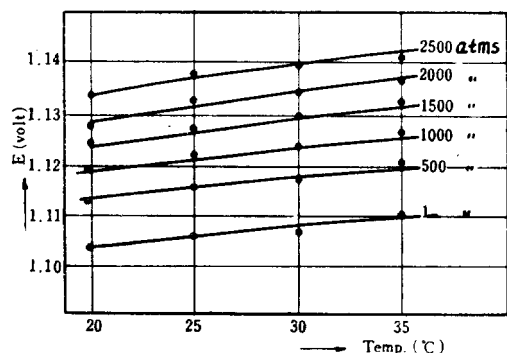|		
1.	Spindle presser	2. Connector
3.	Manometer	4. 6. Valve
5.	Oil vessel	7. Presser vessel
8.	Thermostat	9. DC potentoimeter

Fig. 4.

Fig. 5.

Here, the logarithmic term is thought to be
increasing with pressure since the numerator
increses faster than the denominator of the above

Table 2. The mole concentration of water at integral
values of temperatures and Pressures.

Press. (atms)	Temp. (°C)			
	20	25	30	35
1	55.408	55.339	55.269	55.173
500	56,628	56.542	56.456	56.350
1,000	57.736	57.539	57.423	58.626
1,500	58.597	58.568	58.539	59.538
2,000	59.408	59.272	59.139	60.354
2,500	60.219	60.084	59.949	

equation with pressure because of increasing the
degree of dissociation of the salt. Accordingly,
it is reasonable that the emf of the cell inc-
reases with pressure and temperature.

The G. C. Kennedy's[17] Data. The specific vo-
lumes of liquid water with the pressure and tem-
perature change, were converted into densities,
and the mole concentrations of water were cal-
culated from eq. (14) as shown in *Table 2.*
The mole concentrations of water decreased with
increasing temperature and increased with increa-
sing pressure.

To get the average net change in waters of
solvation (k) before and after dissociation, the
relation of $\left(\frac{\partial E}{\partial P}\right)_T$ vs. $\left(\frac{\partial \log C_{H_2O}}{\partial P}\right)_T$ of the eq.
(13) should be plotted and k calculated from its
slope. In doging so, the relation $E.$ vs. P at
25 °C was calculated by using "the method of
least square"

$$E = -41.63 \times 10^{-10} P^2 + 2.27 \times 10^{-5} P$$
$$+ 1.1048 (\text{volt}). \qquad (26)$$

Also at 25 °C, the following expression is obta-
ined from the relation $\log C_{H_2O}$ and pressure by
means of the same method mentioned above.

$$\log C_{H_2O} = 33.54 \times 10^{-10} P^2 + 2.3159 \times 10^{-5} P$$
$$+ 1.7417 (\text{mole}). \qquad (27)$$

Differentiating eq. (26) and (27) with respect
to pressure (P) at constant temperature (T),
we have the slopes at each pressure. and plot

the relationship of $-\left(\dfrac{\partial E}{\partial P}\right)_T$ and $\left(\dfrac{\partial \log C_{H_2O}}{\partial P}\right)_T$ in the *Fig.* 6.

The graph shown shown in *Fig* 6. showed good lineality of the relation between $-\left(\dfrac{\partial E}{\partial P}\right)_T$ and $\left(\dfrac{\partial \log C_{H_2O}}{\partial P}\right)_{T,}$ and the slope of *Fig.* 6 is equal to 1. 2412. From eq. (13) and the value(1. 2412) of this siope, we have

$$\text{slope}=1.2412=9.208\times10^{-5}kT. \tag{28}$$

The everage net change in waters of solvation of the cell rection (k) of the The conventional ionization constant (K) of the cell reaction at integral pressure eq. (25) at 25°C is calculated to be 41.96 and 25 °C from the eq. (4) is
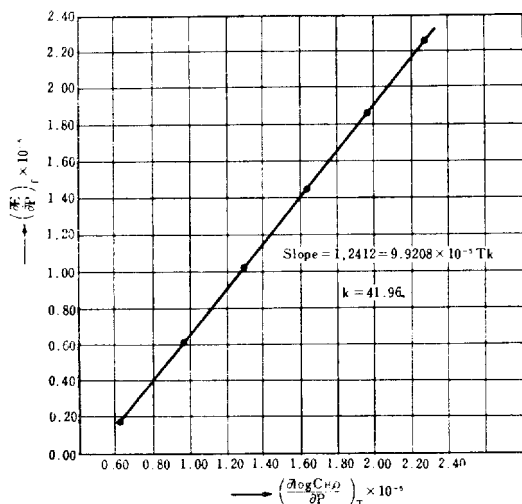

Fig 6.

Table 3. The Conventional ionization constants of the cell reaction at integral pressures

Perss. (atms)	1	500	1,000	1,500	2,000	2,500
$K\times10^{12}$	44.543	11.199	25.754	50.291	63,829	157.778

Table 4. The conventional standard emf of cell at integral pressures

Press. (atms)	1	500	1,000	1,500	2,000	2,500
E° (volt.)	0.9660	0.9776	0.9883	0.9969	0.9999	1.0116

shown in *Table* 3.

The conventional ionization constant(K) increase with pressure, because the degree of dissociation of the salt increases with pressun.

Conventional standard emf of cell (E°) was calculated from 1 to 2500 atms in the eq. (7) and shown in *Table* 4.

E° increases with pressure, because E increases with pressure at constant temperature. The relation of E° *vs.* pressure (P) is shown in *Fig.* 7 and by using the method of least square the following equation is obtained.

$$E=-40.06\times10^{-10}P^2+2.86\times10^{-5}P$$
$$+0.9646(\text{volt.}) \tag{29}$$

Thus, it is possible to get the conventional standard emf of the cell at high pressure. This means that the emf of the cell(E) measured at high pressure and various kind of thermodynamic properties can be calculated as a function of both pressure and temperature and at the same time, the theory of chemical equilibrium of using the emf of the cell can be treated at high pressure as well as at atmospheric pressure.
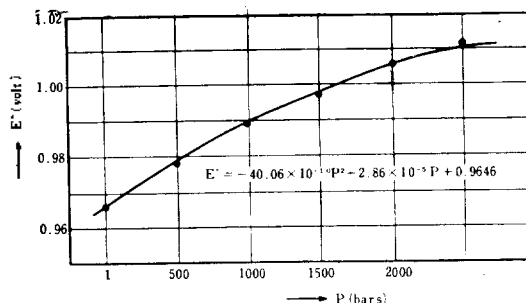
To calculate the partial molal volume change

Fig. 7.

Table 5. The partial molal volume change of the cell reaction at integral pressures at 25

Press. (atms)	1	500	1,000	1,500	2,000	2,500
$-\Delta V^\circ$ (cm₃/mole)	54.45	46.84	39.21	31.58	23.95	16.32

Table 6. The compressibility of water in the cell reaction at integral pressures and 25 °C.

Press. (atm)	1	500	1,000	1,500	2,000	2,500
$\beta \times 10^{-5}$ (mole/atm)	5.31	4.56	3.82	3.08	2.34	1.59

Table 7. The free energy change($\Delta G°$) of the equilibrium state at 25°C and integral Pressure

Press. (atms)	1	500	1,000	1,500	2,000	2,500
$-\Delta G°$ (Kcal/mole)	44.74	45.24	45.77	46.18	46.32	46.84

Table 8. The enthalpy change $H°$ of the equilibium state at 25°C and integral pressure.

Press. (atms)	1	500	1,000	1,500	2,000	2,500
$-\Delta H°$ (Kcal/mole)	44.35	44.78	45.26	45.62	45.70	46.18

Table 9. The entropy change($\Delta S°$) of the equilibrium state at 25° and integral pressure.

Press. (atms)	1	500	1,000	1,500	2,000	2,500
$\Delta S°$ (eu/mole)	1,329	1,513	1,699	1,884	2,067	2,254

($\Delta V°$) of the cell reaction at equilubrium state from the eq. (15), it is necessary to differentiate eq. (29) with respect to pressure at constant temperature. Finding the slope at each pressure. We calculated values of $\Delta V°$ from this slope and have shown those in Table 5.

$\Delta V°$ decreases with increasing pressure is natural because the partial molar volume change ($\Delta V°$) of each chemical species does with increasing pressure. From obtained $\Delta V°$ and k, the compressibility of water(β) is calculated in eq. (23) and shown at Table 6.

That decrease with increasing pressure is the same as was stated about $\Delta V°$ before. $\Delta G°$ is calculated from eq. (21) as the follow.

We have no data of the temperature gradient of the standard emf($E°$) of the cell at atmospheric pressure and caluculate $H°$ and $S°$ in Table 8 and 9 respectively supposing $\left(\frac{\partial F°}{\partial P}\right)_T$ were $\left(\frac{\partial E}{\partial P}\right)_T$.

The facts that $\Delta G°$ and $\Delta H°$ decrease with increasing pressure and $\Delta S°$ increase are described from the aspect of the standard emf ($E°$) of the cell increase with pressure.

Reference

1. G. N. Lewis and M. Randall, J. Amer. Soc., 36, 1969(1914).

2. N. E. Loomis and S. F. Acree, ibid., 38, 2391(1916).

3. J. H. Ellis, ibid., 38, 737(1916).

4. E. Cohen and K. Piepenbroek, Z. Phisk. Chem., 170A, 145(1934)

5. E. U. Franck, J. E. Savolainen and William L. Marshall, The Peview of Scientific Instruments 33, 115~117(1962).

6. Arvin S. Quist and William L. Marshall, J. Phys. Chem., 72, 684(1968).

7. Leroy B. Yeatts and William L. Marshall, ibid., 76, 1053(1972).

8. Lawrence A Dunn and William L. Marshall, ibid., 73, 723(1972).

9. Frank, Z, Phys. Chem. (Frankfurt an Main), 9, 192(1956).

10. W. L. Marshall and A. S. Quist, *Pros. Natl. Acad. Sci. U.S*, **58**, 901(1969).

11. A. S. Quist and W.L. Marshall, *J. Pyhs. Chem*, **72**, 1536(1968).

12. W. L. Marshall, *ibid.*, **76**, 720(1972).

13. W. L. Marshall, *ibid.*, **74**, 346(1970).

14. Duncan A. MacInnes "The Principles of Electrochemistry" P. 178, Dover Publications, Inc.

15. J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 809(1959).

16. B. T. Baliga and E. Whalley, *ibid.*, **55**, 908 (1959).

17. *a*) G. C. Kennedy, W. L. Knight and W.T. Holser, Properties of Water Part III, Specific Volume of Liquid Water to 100°C and 1400 bars; *b*) C. Wayne Buurnham, J. R. Holloway and N. F. Davis, The Specific Volume of Water in the range 1,000 to 8,900 bars, 20° to 900°C.