

- tes", pp. 308, Academic Press, 1982
2. R. M. Barrer, FRS, "Zeolites and Clay Minerals as Sorbents and Molecular Sieves", pp. 35, Academic Press Inc., London LTD., 1978.
 3. R. M. Barrer, FRS, "Hydrothermal Chemistry of Zeolites", pp. 251, Academic Press, 1982
 4. H. W. Kovenhowen and W. H. J. Stork, U. S. Patent, 3,028,395.
 5. W. J. Ball, J. Dwyer, A. A. Garforth, and W. J. Smith, "Studies in Surface Science and Catalysis", **28**, 137 (1986).
 6. R. Szostak and T. L. Thomas, *J. Catal.*, **100**, 555 (1986).
 7. R. Szostak and T. L. Thomas, *J. Chem. Soc., Chem. Commun.*, 113 (1986).
 8. R. M. Barrer and J. F. Cole, *J. Chem. Soc., (A)*, 1516 (1970).
 9. J. A. Rabo, "Zeolite Chemistry and Catalysis", pp. 59, American Chem. Soc., 1976.
 10. J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", 3rd ed., pp. 201, Harper & Row, Publishers, New York, 1983.
 11. A. N. Lazarev, "Vibrational Spectra and Structure of Silicates", pp. 77-85, translated ed., V. C. Farmer, consultants Bureau, New York, 1972.

Free Energy of Ion Hydration

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The influence of temperature and pressure on the free energy of the ion hydration has been considered. The ion radii measured by conductometric method and the saturated dielectric constant cited from other works were used to calculate the free energy in the hydration shell. The Born equation was modified in order to fit in our model. In our model, the environment of ion consists of three regions. The innermost one is the hydration shell in which water is immobilized and electrostricted, the middle one is the one which contains less ordered waters than the bulk medium, and the outermost one is the bulk water which is under the influence of the electric field of ion. Our results for the free energy of ion hydration were compared with those of other attempts. Especially, ΔG_{hyd} of Li^+ ion is considerably too negative in this study at given temperature, comparing with those of other attempts. But ΔG_{hyd} of other ions coincides with each other.

Introduction

The solvation properties of electrolytes in aqueous solution are important in solution chemistry. Especially the ion hydration plays an important role in chemical and biochemical processes. The Born model¹ for the free energy of ion hydration forms the basis for a continuum approach.² The free energy of ion hydration is the reversible work required to charge a conducting hard sphere of radius r , embedded in a polarizable fluid with the relative dielectric constant ϵ_r at constant temperature and pressure and is expressed as

$$\Delta G = \frac{N_A(Ze)^2}{8\pi\epsilon_0 r} (1 - 1/\epsilon_r) \quad (1)$$

Where, N_A , Ze , and ϵ_0 are the Avogadro number, the charge of the ion, and the dielectric constant of vacuum, respectively. As it was shown by Born approximation, the free energy of ion hydration depends upon two parameters, the ionic radius r and the relative dielectric constants ϵ_r of the fluid. Quantitatively speaking, the Born model is rather crude, due to the hard sphere assumption for the ionic solute and the treatment of the solvent as a continuous dielectric medium. According to this model, the free energies of hydration of not only the positively charged ions but negatively

charged ones turn out to be the same when the same values of radii are used. However, such results are highly questionable since the surrounding patterns of water molecules around positive ion and negative one are quite different. Better result may be obtained, if the effective radii of hydrated ion and the dielectric constant of water in regions vicinal to the ion (due to dielectric saturation) are obtained. In fact, because of this, Born equation has been modified by a number of authors.³⁻¹¹

In this paper, we have used the effective hydrated ionic radii obtained from our experimental results¹² and the saturated dielectric constant cited from other works^{9,13} in order to calculate the free energies of ion hydration in the hydration shell and outside of it as well. We have modified the Born equation for the electrostatic free energy of the ion hydration using the effective hydrated ionic radii and the saturated dielectric constants.

Model

The hydration-shell model deduced from our experiment resembles that of the Frank and Wen.¹⁴ In their (or our) model, the environment of ion consists of three regions. The innermost one is the hydration shell in which the water is

immobilized and electrostricted, the middle one is the one which contains less ordered waters than the bulk medium, and the outermost one is the bulk water which is under the influence of the electric field of ion.

In our model, the ion seems to interact with its environment as follows. Firstly, a cavity of radius r_{eff} is formed in water, and then the ion with its hydration shell is inserted into the cavity interacting with the bulk water by means of dispersion and dipole-induced dipole interactions as if it were uncharged. Later the charging process makes the charge effectively large as much as to produce the electric field which causes the dielectric saturation in the hydration shell. The permittivity (or dielectric constant) of the water in the hydration shell is considered to have the effective-local dielectric constant ϵ_{eff} . Since this local effect is different from ion to ion, as is $q(\text{charge})/r(\text{radius})$ ratio, it is reasonable to use the different effective dielectric constants proposed by Noyes.⁵ The dielectric constant of water beyond the distance r_{eff} is the bulk value ϵ obtained by other works.^{15,16}

In the present study, the molar Gibbs energy of ion hydration has been modified as

$$\Delta G_n = 41 - 87(r_{\text{eff}}). \quad (2)$$

ΔG_n (KJ/mol) represents the free energy of a non-polar gaseous neutral solute^{10a} of the same size as a corresponding ion. The constants in Eq. (1) were obtained from the data in ref. 11. r_{eff} (Å) is the effective radius of hydrated ion and is obtained from our experiment (see the next section). The equation of Gibbs energy of the electrostatic interaction in the hydration shell is expressed in refs. 10(a) and 11. But these models in refs. 10(a) and 11 are not adequate in our model because those were one-layer ones. So we modified those in order to fit in our model. Then, generally, the modified Gibbs energy in the electrostatically interactive region, i.e., in the n -layers hydration shell becomes.

$$\Delta G_{e1} = (N_A e^2 / 8\pi \epsilon_0) z^2 \sum_{i=1}^n (1 - 1/\epsilon_{\text{eff}}^i) [(1/r_{i-1} - 1/r_i)]. \quad (3)$$

Where, ϵ_{eff}^i ,¹⁷ r_{i-1} , and r_i are the effective dielectric constant of water in the i th hydration shell and the radius to the $(i-1)$ th and i th layer of water surrounding ion. If we applied Eq. (2) to our model, i.e., $n=2$, ΔG_{e1} becomes

$$\Delta G_{e1} = (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon_1) [(1/r_c - 1/r_1)] + (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon_2) [(1/r_1 - 1/r_{\text{eff}})]. \quad (4)$$

Where, ϵ_1 , ϵ_2 , and r_1 are the effective dielectric constant of water in the first hydration shell, that of water in the second hydration shell and the radius (obtained from the hydration number and rdf results of other works^{16,18}) to the first layer of water surrounding ion, respectively. r_c is the radius of ion obtained from a crystallographic study.¹⁹ In the right-hand side of Eq. (4), the first and the second terms represent the free energy of electrostatic interaction between ion and water in the first hydration shell and that in the second hydration shell, respectively. We assumed that the effective dielectric constants of water in second hydration shell was approximately equal to means value between that in first hydration shell and that in bulk.²⁰

In the mean time, the Gibbs energy beyond the hydration shell becomes,

$$\Delta G_{e2} = (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon) / r_{\text{eff}}. \quad (5)$$

Where, ϵ is the dielectric constant of bulk water. Since in our model the interaction beyond the hydration region is included, the Gibbs energy from the electrostatic interactions becomes

$$\Delta G_{e1+2} = (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon_1) [(1/r_c - 1/r_1)] + (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon_2) [(1/r_1 - 1/r_{\text{eff}})] + (N_A e^2 / 8\pi \epsilon_0) z^2 (1 - 1/\epsilon) / r_{\text{eff}} \quad (6)$$

The contribution of the effects of the ion on the structure of water to the Gibbs energy of the hydration beyond what is already specified by Eqs. (1) and (6) is negligible.¹⁹ Hence the total Gibbs free energy of interaction of the ion with its surroundings in the infinitely dilute solutions is just the sum of the contributions given in Eqs. (1) and (6).

$$\Delta G_{\text{hyd}} = \Delta G_n + \Delta G_{e1+2} \quad (7)$$

Experimental and Calculation

Experimental. LiCl, NaCl, KCl and KBr of the guaranteed reagent grade were obtained from Aldrich Chemicals Co. Ltd. Stock solution of 1.000×10^{-2} M was prepared at 20°C which was then diluted volumetrically to the required concentration at the time of usage. Water was prepared using Millipore purification system and had a specific resistance greater than 1×10^6 ohm-cm.

The conductance bridge of Johns-Joseph type made by Rhode-Schwarz Co. in Germany was used in this study. The dipping cell of Beckmann Co. was used to measure conductivity of electrolyte at atmospheric pressure. But the high pressure conductivity cell made of teflon, platinum, and glass-stopper was manufactured in our laboratory and has the capacity of about 3 ml. The teflon tube is so thin that it can transmit pressure effectively and at the same time isolate the sample completely from mineral oil used as pressure-transmitting fluid.¹² The pressure in the vessel was measured directly by means of a calibrated resistance gauge (Bourdon gauge). The cell constant at atmospheric pressure was determined by using standard solution of 0.01 D KCl²⁰ ($\kappa = 0.0128560$ ohm⁻¹·cm⁻¹). The cells with 1.5346 and 1.5618 cm⁻¹ constant values were used for the measurements.

The changes of concentration of dilute sample solutions by pressure were calibrated using the density data of water.¹⁵ The temperature was controlled by a thermostat of Beckmann Co. to $\pm 0.05^\circ\text{C}$.

Calculations. The limiting equivalent conductances of LiCl, NaCl, KCl, and KBr have been measured by conductometric method in the range of temperature from 20 to 40°C and of pressure from 1 to 2000 bars at 250°C. Those of LiCl, NaCl, KCl, and KBr were already published in ref. 12. The limiting equivalent conductances of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions have been obtained by TATB method.²³

The Stokes' law radii r_s of ions on classical hydrodynamics were calculated from the limiting equivalent conductance of ion and viscosity of water obtained from refs. 15 and 16. However, Stokes' law radii are often inappropriately small because water is not a constant medium. In fact, the radii of the hydrated ions should be greater than that of the water molecules even in a viscous fluid state²⁴. In order to measure

Table 1. Effective Radius, r_{eff} (Å) of Ions in Water

Temp. (°C)	Ion				
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
20	3.81	3.56	3.30	3.30	3.27
25	3.81	3.57	3.31	3.32	3.29
25 ^a	3.82	3.58	3.31	3.32	3.30
25 ^b	2.41	2.18	2.12	2.24	2.31
30	3.85	3.57	3.33	3.33	3.30
35	3.88	3.59	3.35	3.35	3.32
40	3.92	3.61	3.37	3.37	3.34

^aRef. 25. ^bRef. 11.

the deviations of Stokes' radii of small ions, it is desirable to establish a calibration procedure based upon ions whose radii in solution are known, and consequently, upon the crystallographic radii of ions which unhydrated. There are two methods that obtain the effective radius of a hydrated ion. One is Robinson and Stokes method²⁵ which is highly uncertain for ions with Stokes radius less than 2.5 Å,²⁴ and the other is Nightingale method²⁴ with assumption that all of the tetraalkylammonium ions except the tetramethylammonium ion are unhydrated. Nightingale method were used to obtain the effective radius of a hydrated ion in this study.

From the effective radii r_{eff} and crystallographic radii r_c , the volume of hydration shell surrounding ions has been calculated from Eq. (8).

$$V_{sh} = (4/3)\pi(r_{eff}^3 - r_c^3) \quad (8)$$

The hydration number h of ions have been calculated from Eq. (9).

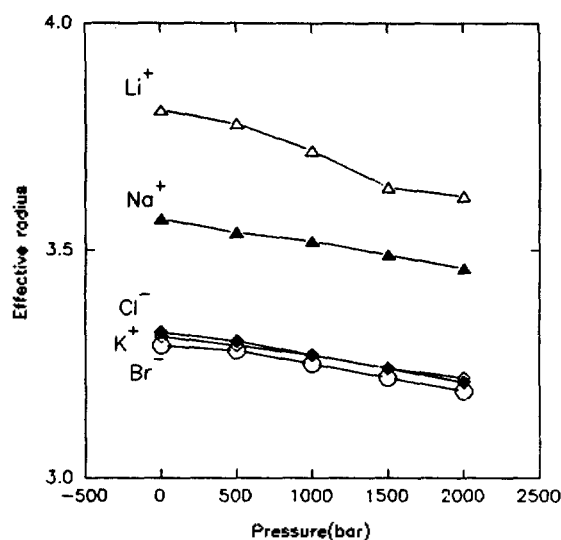
$$h = V_{sh}/V_w \quad (9)$$

where V_w is average volume of one water molecule.¹²

Results and Discussion

The obtained effective radii, r_{eff} , of ions¹² are listed in Table 1 and shown in Figure 1. The values of r_{eff} increase with increasing temperature and decreased with increasing pressure. This trend of r_{eff} was explained by the effect of temperature and pressure on hydration number of ions. If we compare the effective radii in this study at 25°C with the data in ref. 22, those of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions are 3.83, 3.58, 3.31, 3.32, and 3.30 Å in this study and 3.82, 3.58, 3.31, 3.32, and 3.30 Å in ref. 22, respectively. There is a good agreement between these two studies.

The calculated hydration number of ions are listed in Tables 2 and 3. The hydration number of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions increase with increasing temperature. This trend can be explained by the negative hydration of Samoilov.^{12,26} The interested reader should consult the cited refs. for information about the negative hydration. If one compares the hydration number of ions in this study at 25°C with the most probable hydration number of corresponding ion in primary hydration shell¹⁶ listed in Table 2, those of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions are 7.7, 6.2, 4.7, 4.3 and 3.5 in this study and 5 ± 1, 4 ± 1, 3 ± 2, 2 ± 1, and 2 ± 1 in ref.

**Figure 1.** Effect of pressure on the effective radius of ions at 298 K.**Table 2.** Hydration Number (h) of Ions

Temp. (°C)	Ion				
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
20	7.7	6.2	4.7	4.2	3.5
25	7.7	6.2	4.7	4.3	3.5
25 ^a	5 ± 1	4 ± 1	3 ± 2	2 ± 1	2 ± 1
30	7.9	6.2	4.8	4.3	3.6
35	8.1	6.3	4.9	4.4	3.7
40	8.4	6.5	5.0	4.5	3.8

^aRef. 16.**Table 3.** Hydration Number (h) of Ions at 25°C

Press. (bars)	Ion				
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
1	7.7	6.2	4.7	4.2	3.5
1 ^a	—	—	2.5	1.9	—
500	7.8	6.3	4.8	4.3	4.0
500 ^a	—	—	2.6	1.9	—
1000	7.4	6.2	4.7	4.2	3.9
1000 ^a	—	—	2.5	1.9	—
1500	7.2	6.2	4.7	4.2	3.9
1500 ^a	—	—	2.6	1.8	—
2000	7.1	6.1	4.6	4.1	3.7
2000 ^a	—	—	2.4	1.8	—

^aRef. 28.

16, respectively. It can be found that the results of this study agree with Frank-Wen model in ref. 14. The hydration number of ions in this study decreases slightly with increasing pressure. Since all ions are hydrated by electrostatic force and hydrogen bonding, the effect of pressure on hydration number of ions can be explained by the pressure-induced

Table 4. Dielectric Constant of Water (ϵ) and Average Volume of Water Molecule (V_w)

Temp (°C)	20	25	30	35	40
ϵ^a	80.34	78.54	76.78	75.04	73.39
Press. (bar)	1	500	1000	1500	2000
ϵ^b	78.54	80.81	82.88	84.80	86.57
V_w^c (Å ³)	30	29	29	28	28

^aRef. 16. ^bRef. 15. ^cRef. 31.

dehydration suggested by Horne²⁷. If one compares the hydration numbers of K⁺ and Cl⁻ ions in this study at 25°C and 1 bar with those of Nakahara's²⁸, those of K⁺ and Cl⁻ ions are 4.7 and 4.3 in this study and 2.5 and 1.9 in Nakahara's study, respectively. Those of K⁺ and Cl⁻ ions at 25°C and 2000 bars are 4.6 and 4.1 in this study and 2.4 and 1.8 in Nakahara's study, respectively. The results of this study were almost twice as large as those of Nakahara's. These differences generally arise from the differences of obtaining the limiting equivalent conductances of ions and of calibrating the Stokes' radius and the effective radii of ions. In this study, TATB method and Nightingale method have been used to obtain the hydration number of ions at given temperature and pressure. But Nakahara's group chooses (Bu)₄N⁺ as a reference ion and the radii have been calibra-

ted by the correction factor suggested by Nakahara's group.²⁹ Nakahara's group assumed that correction factors are independent on the temperature and pressure.²⁸

From the comparison of hydration numbers among three studies, it was found that the first layer waters and a fraction of the second layer waters are efficiently surrounding the probe ion. From this, we could choose our model needed to obtain the free energy of ion hydration. This two-layers model is coincide with other work.³⁰ Comparing the effective hydrated radii of Na⁺ (3.57 Å) and Cl⁻ (3.32 Å) ions in this study at 25°C and 1 bar with the calculated ion-oxygen (Na⁺; 2.35 Å, Cl⁻; 3.20 Å) and ion-hydrogen (Na⁺; 2.90 Å, Cl⁻; 2.20 Å) distances obtained by using only the first hydration shell at 300 K and 1 bar in ref. 30 and comparing the hydration number (6.2) and the effective radius (3.57 Å) of Na⁺ ion in this study at 25°C and 1 bar with that (4.9) and the minimum value of first *rdf* peak (3.4 Å) of Na⁺ ion in the first hydration shell in ref. 18(b), we think that our model seems to be reasonable.

According to our model, we calculated the free energy of ion hydration. First, ΔG_h has been calculated using Eq. (1) at constant temperature and pressure. These values decrease with increasing temperature and increase with increasing pressure. The calculated values of ΔG_h has been within the known range¹¹. The dielectric constants of water^{15,16} needed to calculate ΔG_{cl+2} at given temperature and pressure and the average volume of water at a given pressure³¹

Table 5. Effective Dielectric Constant of Water (ϵ_{eff}) and Crystallographic Radius (r_c) of Ion at 25°C

Temp. (°C)	Ion									
	Li ⁺		Na ⁺		K ⁺		Cl ⁻		Br ⁻	
	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2
20	2.85	41.60	2.37	41.36	2.88	41.61	12.70	46.52	13.58	46.96
25	2.79	40.67	2.32	40.43	2.82	40.68	12.42	45.48	13.28	45.91
30	2.78	40.55	2.31	40.31	2.81	40.56	12.38	45.34	13.24	45.77
35	2.67	38.86	2.22	38.63	2.69	38.86	11.87	43.45	12.69	43.86
40	2.61	38.00	2.17	37.78	2.64	38.01	11.61	42.50	12.41	42.90

Press. (bars)	Ion									
	Li ⁺		Na ⁺		K ⁺		Cl ⁻		Br ⁻	
	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2
1	2.79 ^a	40.67	2.32 ^a	40.43	2.82 ^a	40.68	12.42 ^a	45.48	13.28 ^a	45.91
500	2.87	41.85	2.39	41.60	2.90	41.86	12.78	46.79	13.66	47.24
1000	2.94	42.92	2.45	42.67	2.98	42.93	13.11	48.00	14.01	48.45
1500	3.01	43.91	2.50	43.65	3.04	43.92	13.41	49.10	14.34	49.57
2000	3.08	44.83	2.56	44.56	3.11	44.84	13.68	50.13	14.64	50.60

	Ion				
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
r_c^b (Å)	0.69	1.02	1.38	1.81	1.96

^aRef. 13. ^bRef. 19.

Table 6. Molar Gibbs Energy of Ion Hydration ΔG_{hyd} (KJ/mol)

Temp. (°C)	Ion				
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
20	-671.1	-434.0	-360.2	-329.3	-305.0
25	-665.6	-430.1	-358.3	-329.1	-304.9
30	-665.1	-429.1	-358.1	-329.2	-304.9
35	-654.5	-421.5	-353.9	-328.7	-304.7
40	-648.5	-417.0	-352.1	-328.5	-304.6

Table 7. Molar Gibbs Energy of Ion Hydration at 25°C ΔG_{hyd} (KJ/mol)

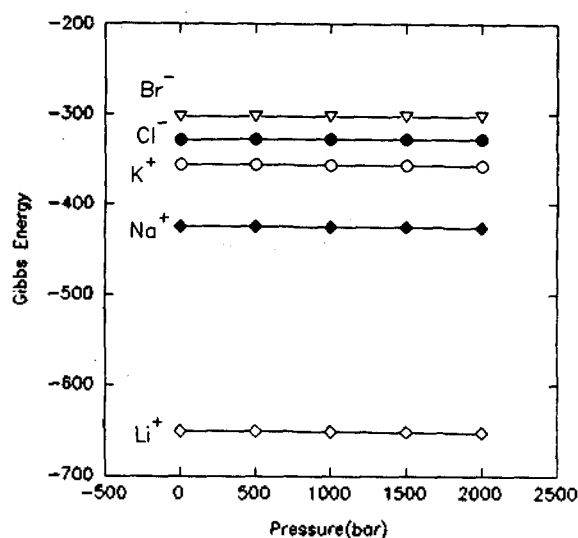
	Ion				
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
Noyes ^a	-511.0	-411.5	-337.1	-318.4	-289.5
Symons ^b	-514.2	-408.4	-340.2	-317.1	-289.5
Stokes ^c	-	-432.6	-357.7	-287.0	-282.8
Abraham ^d	-	-412.5	-338.1	-286.2	-257.3
Berendsen ^e	-	-431.4	-348.6	-239.2	-228.2
Friedman ^f	-	-419.2	-346.0	-325.1	-311.3
Bucher ^g	-511.2	-411.0	-337.7	-317.3	-303.0
Marcus ^h	-475.5	-365.0	-295.0	-340.0	-315.0
This work	-665.1	-430.1	-358.3	-329.2	-304.9

^aRef. 5. ^bRef. 33. ^cRef. 6. ^dRef. 10(a). ^eRef. 1. ^fRef. 34. ^gRef. 9. ^hRef. 11.

were presented in Table 4. The effective dielectric constants of waters¹³ surrounding ion and the crystallographic radii of ions¹⁹ were listed in Table 5.

Second, ΔG_{e1+2} has been also calculated using Eq. (6) at constant temperature and pressure. ΔG_{e1+2} of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions at 25°C and 1 bar in this study are -673.5, -440.0, -370.5, -341.2 and -317.3 KJ/mol, respectively. While ΔG_{e1} of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions at 25°C and 1 bar in ref. 13 are -515.9, -492.0, -453.5, -325.9 and -298.3 KJ/mol, respectively. These values in ref. 13 were obtained by the electrostatic polarization potential, expressed as a function of central charge concept and the critical radii, and calculated ΔG_{e1} base on the Born formula. On the other hand, ΔG_{e1} of Li⁺, Na⁺, K⁺, Cl⁻ and Br⁻ ions at 25°C and 1 bar in ref. 5 are -510.9, -411.7, -336.8, -318.4 and -289.5 KJ/mol (obtained from convention that hydrogen ion has zero value), respectively. The difference of ΔG_{e1+2} in three studies resulted from the method and assumption used to obtain ΔG_{e1+2} of ions.

The ΔG_{hyd} of ions (obtained using Eq. (7) at various temperatures) were listed in Table 6. Those of Li⁺, Na⁺, K⁺, Cl⁻, and Br⁻ ions slightly increase with increasing temperature. Though the range of temperature is different, the trend of temperature of the ΔG_{hyd} of corresponding ions was similar with that of Abraham³². Since the Born equation was imperfect, many workers have attempted to improve it to determine the ΔG_{hyd} of ions. The results of other workers are presented in Table 7 together with the results of this study. The ΔG_{hyd} of Li⁺ ion obtained from this work is much nega-

**Figure 2.** Effect of pressure on the Gibbs free energy of ions hydration at 298 K.

tively larger than that of others. This is because the number of water surrounding Li⁺ ion is bigger than those of other workers. Although the different assumptions were used to obtain the ion radii the effective dielectric constants of water surrounding ion, the ΔG_{hyd} 's coincide with each other except Li⁺ ion. As shown in Figure 2, the ΔG_{hyd} of Li⁺, Na⁺, K⁺, Cl⁻ and Br⁻ ions at 25°C decrease with increasing pressure. This may be due to the decrease of the hydration number of ions with increasing pressure.

References

1. M. Born, *Z. Phys.*, **1**, 45 (1920).
2. J. D. Bernal and F. D. Foeler, *J. Chem. Phys.*, **1**, 515 (1933).
3. T. P. Straatsma, H. J. C. Berenden, and J. P. M. Postma, *J. Chem. Phys.*, **85**, 6720 (1986).
4. W. M. Latimer, K. S. Pitzer, and C. M. Slankys, *J. Chem. Phys.*, **7**, 108 (1939).
5. R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 514 (1962).
6. R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).
7. H. Block and S. M. Walker, *Chem. Phys. Lett.*, **19**, 363 (1973).
8. A. A. Rashin and B. Honig, *J. Phys. Chem.*, **89**, 5588 (1985).
9. M. Bucher and T. L. Porter, *J. Phys. Chem.*, **90**, 3406; 3411 (1986).
10. (a) M. H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. I*, **74**, 1604, 2858 (1978); (b) R. H. Wood and D. E. Delaney *J. Phys. Chem.*, **72**, 4651 (1968); (c) J. H. Saylor and R. Battino *J. Phys. Chem.*, **62**, 1334 (1958); (d) E. Wilhelm, R. Battino, and R. J. Wilcock, *Chem. Rev.*, **77**, 219 (1977).
11. Y. Marcus, *J. Chem. Soc., Faraday Trans. I*, **87**, 2995 (1991).
12. (a) H. S. Kim, D. S. thesis, Kyungbook National University, 1991; (b) J. U. Hwang, H. S. Kim, S. K. Cha, and E. H. Park, *J. Kor. Chem. Soc.*, **35**, 443 (1991); (c) J. U. Hwang, J. J. Chung, and H. S. Kim, *J. Kor. Chem. Soc.*,

- 36, (1992).
13. R. R. Contreras and A. J. Aizman, *Int. J. Quantum Chem. Quantum. Chem. Symp.*, **25**, 281 (1991).
 14. H. S. Frank, and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).
 15. F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962).
 16. J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry" Vol. 1 Plenum Press, New York, 1970.
 17. D. Morales-Lagos and J. S. Gomez-Jeria, *J. Phys. Chem.*, **95**, 5308 (1991).
 18. (a) J. Chandrasekhar, D. C. Spellmeyer, and W. L. Jorgensen, *J. Am. Chem. Soc.*, **106**, 903 (1984); (b) Kwang S. Kim, *Chem. Phys. Lett.*, **156**, 261 (1989); (c) P. Cieplak and P. Kollman, *J. Chem. Phys.*, **11**, 6761 (1990); (d) E. Guardia and J. A. Padro, *J. Phys. Chem.*, **94**, 6049 (1990); (e) L. X. Dang, *J. Chem. Phys.*, **9**, 6970 (1992).
 19. L. Pauling, *The Nature of the Chemical Bond and Structure of Molecules and Crystals*, 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.
 20. M. H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. I*, **76**, 1219 (1980).
 21. A. Ben-Naim, *Water and Aqueous Solutions*, Plenum Press, New York, ch. 7 (1974).
 22. J. E. Lind, JR. James, J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).
 23. J. I. Kim, *J. Phys. Chem.*, **82**, 191 (1978).
 24. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions" Academic Press, Inc., New York, N. Y., 1955.
 25. JR., E. R. Nightingale, *J. Phys. Chem.*, **63**, 1381 (1959).
 26. (a) O. Ya. Samoilov, *Structure of Aqueous Electrolyte Solutions and Hydration of ions*, p. 74, Consultants Bureau, New York, 1965; (b) E. S. Amis and J. F. Hinton, "Solvent Effects on Chemical Phenomina" p. 10, Academic Press, New York, 1973.
 27. R. A. Horne, *Advances in High Pressure Research*, Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London, 1969.
 28. M. Nakahara, K. Shimizu, and J. Osugi, *J. Rev. Phys. Chem. Japan*, **42**, 12 (1972).
 29. M. Nakahara, K. Shimizu, and J. Osugi, *J. Nippon Kagaku Zasshi*, **92**, 785 (1971).
 30. L. Dang, J. Rice, J. Caldwell, and P. A. Kollman *J. Am. Chem. Soc.*, **113**, 2481 (1991).
 31. M. Nakahara, K. Shimizu, and J. Osugi, *J. Rev. Phys. Chem. Japan*, **40**, 1 (1970).
 32. M. H. Abraham, E. Matteoli, and J. Liszi, *J. Chem. Soc., Faraday Trans. I*, **79**, 2781 (1983).
 33. M. J. Blandamer and M. C. R. Symons, *J. Phys. Chem.*, **67**, 1304 (1963).
 34. H. L. Friedman and C. V. Krishnan, in *Water a Comprehensive Treatise*, Edited by F. Franks, Plenum, New York, 1973.

A Study on Ni-H, Pd-H, and Pt-H Systems by Cluster Orbital Method

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As an application of the cluster orbitals proposed previously, nickel-, palladium-, and platinum-hydrogen systems are studied. Density of states, projected density of states, HOMO levels, and stabilization energies are calculated and compared with those obtained by extended Hückel method for small clusters. These calculations are extended to large clusters to find the size dependence of several physical quantities. Reduced overlap populations are also calculated to clarify the charge transfer phenomena reported earlier. The calculated physical quantities show no dependence on the cluster size. It is also found that the charge transfer occurs due to the intrinsic character of palladium, not due to the edge effect which may be present in small clusters.

Introduction

It has been reported previously¹, from extended Hückel (EH) calculations, that hydrogen atoms in palladium cluster are stabilized remarkably compared with those in nickel or platinum. It was also found that charge transfer from metal to hydrogen is more pronounced in palladium cluster than in nickel and platinum. These phenomena were interpreted as being either due to the intrinsic character of palladium or due to the edge effect which may be present in small

clusters. The clusters used for the calculations, however, were too small (with less than a hundred atoms) to show the edge effect properly. So it is necessary to consider large clusters to identify the possible edge effect which may be present in small clusters. Large clusters (say, clusters with more than a hundred or so atoms), however, cannot be treated by the EH method used earlier.

In the earlier work², it has been studied how to obtain analytic solutions of face-centered cubic (f.c.c.) clusters with arbitrary size. Though the shape of the clusters has been