# *Studies on Some Physico-Chemical Properties of Ion-Exchange Resin. I. Heat of Wetting*

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## Introduction

Recently, as an ion-exchange resin has been of great importance in its application in the field of chemistry and chemical engineering, it has now come to be noticed also by many physical chemists as a typical sample of an insoluble high-polymeric electrolyte. Because of its having both a high-polymeric and electrolytic nature, ion-exchange resin seems to have many characteristic properties, one of which is, unlike other high-polymers, the rapid and reproducible swelling in water, which is seen remarkably at the low cross-linked resin, while it is little seen at the high cross-linked resin. In both cases, if the sample has been dried enough, considerable heat is evolved at the moment when it is immersed in water. The author, in this paper, attempted to investigate this phenomenon as a first approach to the fundamental nature of ion-exchange resin. The measurements were made on various forms and states of some cation and anion-exchange resins, and it was found that the amounts of heat evolved depended largely on their forms in such a way that the sequence with the latter was almost parallel with the series of the heats of hydration of the ions. Theoretical considerations were also attempted with the adoption of the appropriate values for the heats of hydration of ions and some assumptions on the dry state of resion.

## Experimental Procedure

**Samples Used.** Samples used are classified into three types; that is, the strongly acidic cation-exchange resins, the weakly acidic cation-exchange resin, and the strongly basic anion-exchange resins.

The first are polystyrene-divinylbenzene sulfonic acid exchangers and are also classified into the following three types according to their cross-linkage. The lowest cross-linked one is easily made from polystyrene by sulfonation with chlorsulfonic acid. The other two are commercial, more or less highly cross-linked, "Amberlite IR-120" and "Amberlite IR-112," whose cross-linkage is said to be 8 % to 10 % and about 5 % divinylbenzene (DVB), respectively.

As a sample of the weakly acidic resin, carboxylic "Amberlite IRC-50" was used. It is a copolymer of methacrylic acid and about 10 % DVB.

Anion-exchange resins used, commercial "Amberlite IRA-400" and "Amberlite IRA-410," are quarternary ammonium salts with the network structures of polystyrene-divinylbenzene.

About 1 g. to 3 g. of resin was used for each run. Well-conditioned, uniform-sized (about 100 Meshes) resin was taken in a column, through which the solutions containing the concerning ion of about ten times as much as the exchange capacity of the resin bed were passed; then it was washed by distilled water, except in the cases described below, till the effluent was freed from the regenerant. In the case of the salt form of carboxylic resin, the washing was made by dilute alkali of about 0.001 N, lest the adsorbed ions might be hydrolyzed[1]. This care was also given in the case of anion-exchange resin, where the exchange was more easily obtained at a lower *p*H range. The drying of samples was done first in an air-oven, then in a desiccator, finally in a test tube with a glass joint stopper in an Abderhalden's dryer at the boiling temperatures of alcohols or water under the reduced pressure of about 0.02 mm Hg. It took from a few days to sometimes about twenty days for the samples to have the constant weights within 1 mg.

The partially desulfonated resins were prepared as follows: the synthesized resin was boiled for about one week with the mixture of conc. sulfuric acid and an almost equal volume of water, at about 150°C. The sample was blackened by this treatment, but the decrease in the exchange capacity was not so great as expected, showing the stability of this sort of resin.

The measurements on the partially wetted samples were made only on acid and sodium forms of the strongly acidic resins, which were prepared either by partial desiccating of resin or by moistening the completely dried resin with damp air. The contents of water in the samples were easily determined by titrating the exchange capacities of resins by column or batch method, and the values obtained agreed with those by the change of weight with drying or wetting.

**Calorimetric Measurement**. Fig. 1 shows the experimental apparatus. When the temperature of the calorimeter reached about 18°C, the readings of the Beckmann thermometer were begun at intervals of 30 seconds with the constant stirring by the stirrer S. Then the samples was carefuly and rapidly thrown from the test tube reserved at the thermostat into the water through the hole C of the vessel. The temperature rise caused by the wetting of the resin occurred immediately after that, sometimes with a noise of its decrepitation. Soon after the temperature-time diagram became flat, another temperature rise which was caused by introducing an electric current through the heater H for some seconds was added to determine the whole heat capacity. This state of matters was shown in a diagram such as Fig. 2, in which these temperature changes were both in the order of 0.1°C to 1.5°C. By determining the weight of samples, the value of the heats of wetting was expressed in cal. per gram, as well as in kcal. per equivalent after the measurement of exchange capacity.

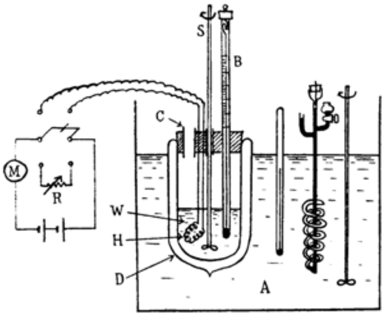

Fig. 1
A: thermostat. B: Beckman thermometer. D: Dewar vessel. S: a plastic stirrer. C: a hole. W: about 180 cc. water. H: a heater. R: resistance box almost equalled with the resistance of the heater. M: a calibrated ammeter (1 amp. range).

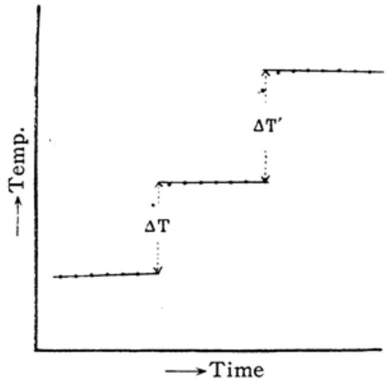

Fig. 2

**Exchange Capacity**. Ordinarily after the calorimetric measurements were done by the above mentioned procedure, the exchange capacity of the resin, i.e., the number of exchange sites per unit, was measured by the column method. In the strongly acidic resins, each salt form was reduced to hydrogen form by the use of 4 N hydrochloric acid as regenerant and was completely washed by distilled water, then by passing the sufficient amount of neutral sodium chloride solution the hydrogen ion that was driven into the effluent was titrated by a standard alkali. In the case of weakly acidic resins, the measure-

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[1] M. Honda, *J. Chem. Soc. Japan* (Pure Chem. Sect.), **71**, 183, 440 (1950), *Japan Analyst*, **1**, 120 (1952).

ments were made by column or batch method, where alkaline, instead of neutral, solution was used to obtain a complete exchange and the washing was also made by dilute alkali.

At the anion exchange resins, the reduced state was selected at the chloride form, and the titration was performed by Mohr's method.

## Results and Discussion

The results obtained are shown in Table I and Fig. 3. From these data it is seen at once as follows: that the values of the heat of wetting of ion exchange resin in general are considerably great as compared with the other high polymers such as starch (about 30 cal./g.)[2], and that there is a remarkable difference between them according to their forms. The sequence at the strongly acidic resin, that is, the fact that the more the valency of the ion or the higher the positon of the ion in the group, the greater is the value of the heat, coincide with the lyotropic series of ion, which undoubtedly has an important relation to the hydration of ions. The degree of difficulty in the dehydration of resin, namely, the period required for the resin to be completely dried in Abderhalden's dryer, was also consistent with this series. Thus the aluminium or magnesium form of this sort of resin was found to have the greatest heat evolution, which was contrary to the result mentioned in a review[3].

As the cation exchange resins were comparatively stable, even the treatment at 100°C did not seem to bring any serious effects, except only that some change of color (getting brown) took place at the hydrogen form, but without any change of exchange capacity. The anion exchange resins were so unstable that they decomposed more or less with a peculiar smell at comparatively low temperatures, especially at the hydroxyl ion form, which lost almost all its capacity by the drying at 65°C.

The results of the weakly acidic type resin were very interesting from the following respects. That is, the largest heat evolution per unit weight was seen with this sort of resin, and the position of the hydrogen form was much lower than that of the other forms, compared with the results of strongly acidic resins. The latter fact may be due to the undissociative nature of the hydrogen atom of the weakly acidic carboxylic group, and the value suggests the magnitude of the hydrogen bond between this hydrophylic radical and the water molecules.

In comparison with the great dependence on the variety of adsorbed ions, the heats of wetting seem scarcely to depend on the cross-linkage as far as this experiment is concerned. Only in the case of the hydrogen form of sulfonic acid type resin an effect just like this was noticed above the experimental error, that is, there was some difference depending on the cross-linkage. However, this probably is accounted for by the considerably high value of heat of dilution of hydrogen ion, and not by the difference of degree of swelling. Thus, such a rather rough measurement as this could not pursue "the swelling heat", which, even if it really exists, must be very small, because the swelling is naturally a phenomenon greatly related rather to the entropy change than to the enthalpy change.

The attempt to find any dependence on the exchange capacity led to the measurement on the desulfonated resin, where although the decrease in the exchange capacity by this method was attained to some extent, the accompanying carbonization of the resin seemed to make the matter complicated.

The calculated values of exchange capacity in a salt form of cation exchangers were derived from the standard hydrogen form by the following formula:

$$E_{\mathrm{MR}}=\frac{E_{\mathrm{HR}}}{1+E_{\mathrm{HR}}\,(m/z-1)}\ (m\text{ eq. per g.})\quad(1)$$

where $E_{\mathrm{MR}}$ is exchange capacity of the concerned salt form (MR), $E_{\mathrm{HR}}$ of acid form (HR), and $m$ and $z$ are molecular weight and valency of the adsorbed ion, respectively.

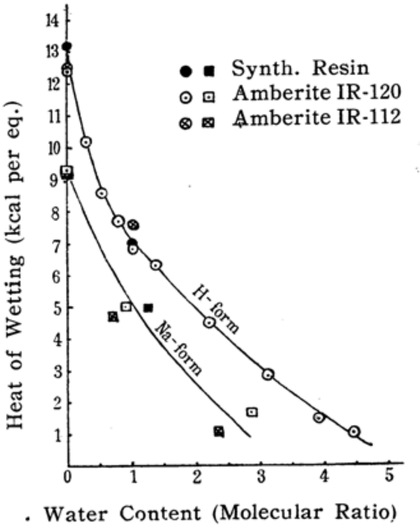

Fig. 3

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[2] T. Nakagawa, This Bulletin, **26**, 169 (1953).

[3] G. E. Boyd, *Ann. Rev. of Phys. Chem.* **2**, 306 (1951).

TABLE I

THE HEAT OF WETTING OF ION EXCHANGE RESIN

| Species of resin | Adsorbed ion form | Drying data Temperature | period | Heat of wetting | | Exchange capacity obs. | capacity calc. | Apparent wet swollen volume in water |
|---|---|---|---|---|---|---|---|---|
| | | (°C) | (days) | (cal./g.) | (kcal./eq.) | | (meq/g.) | cc./g. |
| Synthetic | | | | (Strongly Acidic Cation Exchange Resin) | | | | |
| Resin | Al | 100 | 20 | 83.8 | 19.3 | 4.15 | 4.34 | |
| 〃 | Mg | 100 | 20 | 82.5 | 19.7 | 4.20 | 4.28 | |
| 〃 | H | 100 | 5 | 58.7 | 13.1 | 4.49 | (4.50) | 10 |
| 〃 | H | 78 | 7 | 59.4 | 13.2 | 4.50 | (4.50) | |
| 〃 | Ca | 100 | 20 | 51.0 | 12.3 | 4.02 | 4.15 | |
| 〃 | Li | 78 | 5 | 45.3 | 10.3 | 4.24 | 4.38 | |
| 〃 | Ba | 78 | 10 | 35.8 | 10.4 | 3.29 | 3.44 | |
| 〃 | Na | 78 | 5 | 37.2 | 9.1 | 4.08 | 4.09 | |
| 〃 | K | 78 | 4 | 18.1 | 4.8 | 3.77 | 3.84 | |
| 〃 | $NH_4$ | 78 | 3 | 17.6 | 4.2 | | 4.18 | |
| 〃 | Rb | 78 | 5 | 13.5 | 4.3 | 3.12 | 3.26 | |
| Amberlite | | | | | | | | |
| IR-120 | H | 78 | 5 | 55.9 | 12.4 | 4.50 | (4.50) | 2.3 |
| 〃 | Na | 78 | 5 | 37.8 | 9.3 | 4.08 | 4.09 | |
| 〃 | K | 78 | 5 | 22.7 | 5.9 | 3.84 | 3.84 | |
| Amberlite | | | | | | | | |
| IR-112 | H | 78 | 4 | 56.3 | 12.5 | 4.48 | (4.50) | 5.4 |
| 〃 | Na | 78 | 3 | 37.7 | 9.2 | 4.16 | 4.09 | |
| 〃 | K | 78 | 3 | 18.3 | 4.8 | 3.75 | 3.84 | |
| Desulfonated | H | 78 | 5 | 55.6 | 14.6 | 3.81 | (3.81) | 8.5 |
| Resin I | Na | 78 | 5 | 37.8 | 10.6 | 3.56 | 3.51 | |
| Desulfonated | H | 100 | 5 | 60.5 | 14.1 | 4.30 | (4.30) | 9.0 |
| Resin II | Na | 100 | 5 | 34.9 | 8.7 | 3.94 | 3.94 | |
| Amberlite | | | | (Weakly Acidic Cation Exchange Resin) | | | | |
| IRC-50 | Ca | 78 | 20 | 122 | | 4.8 | 7.9 | |
| 〃 | Na | 78 | 8 | 113.5 | 15.3 | 7.4 | 7.7 | |
| 〃 | Na:H=2:3 | 78 | 6 | 61.6 | 7.6 | 8.1 | 8.6 | |
| 〃 | H | 100 | 8 | 30.7 | 3.2 | 9.6 | (9.35) | 5 |
| 〃 | H | 78 | 3 | 30.4 | 3.3 | 9.1 | (9.35) | |
| Amberlite | | | | (Strongly Basic Anion Exchange Resin) | | | | |
| IRA-410 | Cl | 78 | 4 | 17.0 | 4.6 | 2.8 | | |
| 〃 | $NO_3$ | 65 | 5 | 7.3 | 2.5 | 2.9 | | |
| Amberlite | | | | | | | | |
| IRA-400 | $SO_4$ | 56 | 20 | 41.8 | 14 | 3.0 | | |
| 〃 | $CH_3COO$ | 56 | 4 | 37.4 | 11.4 | 3.3 | | |
| 〃 | I | 56 | 3 | 12.9 | 4.6 | 2.8 | | |

*Parentheses show the standard values selected for calculating the exchange capacity of other forms by Eq. 1.

The observed and calculated values of the exchange capacity were as a whole in good agreement, except the tendency that the former were a little less than the latter. This may be accounted for as follows. (1). Incomplete drying or impurity in reagents. (2). Incomplete regeneration may be probable at the measurement of exchange capacity for the ions which have higher selectivity than hydrogen. (3). For polyvalent ion forms, the occurrence of basic ion such as $Mg(OH)^+$ may increase the apparent equivalent of the ion.

The measurement of the partially wetted samples also gave a very interesting result. As is shown in Fig. 3, at the hydrogen form of strongly acidic resins, about five water molecules per one exchange radical were found to be involved in the heat of wetting, the greatest part of which could be attributed to the hydration of the hydrogen ion. The inflection observed on the curve at the point of one water molecule per one exchange radical may be a proof of the strong attraction between the bare hydrogen ion and one water molecule, forming the hydronium ion ($H_3O^+$). Considering the fact of little dependence on the cross-linkage, this number, about five water molecules per one hydrogen ion, might be said to be the hydration number of the hydrogen ion. The corresponding number for the sodium ion was found to be about three. The author believes that this can be one of the methods to estimate the hydration number of ions. On the other hand, from the wet swollen volume per gram of strongly acidic resin, the resin phase may be regarded as a concentrated solution of about 5 N for IR-120 and 0.5N for synthetic resin. These correspond to the fact that there exist from about ten to one hundred water molecules per one exchange radical, and we may say that the above mentioned five molecules are the bound water and the other are the interstitial water of hydrogen form of this resin.

The following are theoretical considerations on the heat of wetting of sulfonic acid type cation exchanger. The heat of wetting is regarded to be the negative value of the enthalpy change in wetting, $\Delta H_{\mathrm{WET}}$, which is the difference of heat content when the completely dried state of resin is brought to the wetted state. Now, as the model which is shown in Fig. 4, this process may be divided hypothetically into the four steps. (1). The original dried sample is dissociated into fragments in a vacuum, so as for each ion pair as well as the links between structurally bound negative radicals to be separated infinitely. The enthalpy change at this stage is the sum of $\Delta H_{\mathrm{D}}$, due to the dissociation of ion pairs, and $\Delta H_{\mathrm{B}}$, which concerned with the energy required to break the bonds of the polymer network. (2). Then the completely dissociated ions (both cation and radical anion) are brought from the vacuum into the water, when the hydration of ions takes place. The enthalpy change here is caused by the hydration of both ions, $\Delta H_{\mathrm{HYD}}$. (3). Thirdly, the wetted yet infinitely separated ions are concentrated as far as the concentration which corresponds to the swelling state of resin. The accompanying enthalpy change is the negative value of that of dilution from the concentration to the infinite dilution, $\Delta H_{\mathrm{DIL}}$. (4.) Finally, while the concentration of ions are reserved constant on the other hand, the recombination into the swollen resin state takes place. Then the enthalpy change involved is only one term, which is required to combine the separated polymer bonds, thus giving-$\Delta H_{\mathrm{B}}$, just the negative value of the term mentioned at the first step. After all, the change in heat content by wetting is expressed as follows:

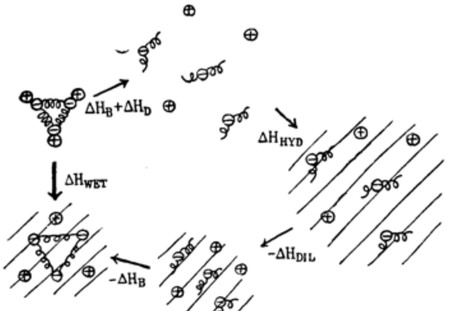

Fig. 4

$$\Delta H_{\mathrm{WET}}=\Delta H_{\mathrm{D}}+\Delta H_{\mathrm{HYD}}-\Delta H_{\mathrm{DIL}}, \quad \ldots(2)$$

in which $\Delta H_{\mathrm{DIL}}$, something similar to the heats of dilution of a few normal solution of usual salts or acids, being only 1 or 2 kcal. per mol at the most, can be neglected at the first approximation, as is compared with the order of about 100 kcal. or much more of $\Delta H_{\mathrm{HYD}}$. Then,

$$\Delta H_{\mathrm{WET}}=\Delta H_{\mathrm{D}}+\Delta H_{\mathrm{HYD}}. \quad \ldots\ldots\ldots(3)$$

As for the energy of hydration of ions, although we have several studies in connection with the ionic radii or hydration numbers, it seems that a complete interpretation with relation to the actual hydrated radii of ions has not yet been obtained, but that only semi-empirical formula originated by Born[4] are still now prevailing[5,6]. The author, too, chose the following formula presented by Latimer[5] as the values of $\Delta H_{\mathrm{HYD}}$.

$$\Delta H_{\mathrm{HYD}}=\frac{-Nz^2e^2}{2(r_{\mathrm{i}}+\mathrm{b})}\left(1-\frac{1}{D}-\frac{T}{D^2}\frac{dD}{dT}\right)$$

c.g.s.e.s.u. per mole, ......(4)

where $N$ is Avogadro's number,
$e$, charge of electron,
$z$, valency of ion,
$r_{\mathrm{i}}$, crystal ionic radius of ion,
$b$, correction value,
$D$, dielectric constant of medium, and
$T$, absolute temperature.

Inserting known figures at room temperature into Eq. 4, one obtains,

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[4] M. Born, *Z.f. Physik.* **1**, 45 (1920).

[5] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

[6] K. B. Yatsimirskii, *J. Gen. Chem.* (U. S. S. R.), **17**, 2019 (1947), *C. A.* **42**, 4809, (1948).

$$\Delta H_{\mathrm{HYD}} = -\frac{165\, z^2}{r_i+b} \text{kcal. per mol.} \quad \ldots(5)$$

where $r_i$ is expressed in Å. The numerical constants b, which have a serious effect on $\Delta H_{\mathrm{HYD}}$, were chosen 0.85 for monovalent cations except hydrogen ion, as was done by Latimer[5]. As he did not give the value for hydrogen, $\Delta H_{\mathrm{HYD}}$ for this ion was taken from the Fajans' value, 255 kcal. per mol.[7]. b's were chosen 0.8 for divalent and trivalent cations and 0.3 for anions, respectively, followed by Yatsimirskii[6]. Thus the $\Delta H_{\mathrm{HYD}}$ for cation is shown in the third column in Table II. The value of $\Delta H_{\mathrm{HYD}}$ for sulfonic acid anion with polymer fragments was arbitrarily assumed to be 40 kcal. per eq., which corresponds to an ionic radius of 3.82 Å according to Eq. 5. As the following discussion refers to, the "true ionic radius of sulfonic acid group" may be assumed to have the value, 1.40 Å, for which, according to Eq. 5, $\Delta H_{\mathrm{HYD}}$ is calculated to be 97 kcal. per Eq. The discrepancy in these values might be interpreted as follows: the attachment of the extra polymer chain may enclose the sulfonic radical, resulting the increase in effective radius; or the hydration of the sulfonic acid group is hindered sterically by the polymer network. The fourth column in Table II is the sum of $\Delta H_{\mathrm{HYD}}$ for cation and 40 kcal.

TABLE II

THEORETICAL CONSIDERATION ON THE HEAT OF WETTING OF SULFONIC ACID TYPE CATION EXCHANGE RESIN

| Ion Species | Crystallographic Ionic Radii* Å | $\Delta H_{\mathrm{HYD}}$ for cation kcal./eq. | $\Delta H_{\mathrm{HYD}}$ total " | $\Delta U$ " | $\Delta H_{\mathrm{D}}$ calc. " | $\Delta H_{\mathrm{WET}}$ calc. " | $\Delta H_{\mathrm{WET}}$ obs. " |
|---|---|---|---|---|---|---|---|
| H | (0) | −255 | −295 | | 335 | +40 | −13.1 |
| Li | 0.60 | −121.2 | −161 | 166 | 149 | −12 | −10.3 |
| Na | 0.95 | − 94.6 | −135 | 141 | 127 | − 8 | − 9.2 |
| K | 1.33 | − 75.8 | −116 | 122 | 110 | − 6 | − 4.8 |
| Rb | 1.48 | − 69.2 | −109 | 115 | 104 | − 5 | − 4.3 |
| Mg | 0.65 | −228 | −268 | 283 | 255 | −13 | −19.7 |
| Ca | 0.99 | −189 | −229 | 243 | 218 | −11 | −12.3 |
| Ba | 1.35 | −154 | −194 | 211 | 190 | − 4 | −10.4 |
| Al | 0.50 | −382 | −422 | 425 | 383 | −39 | −19.3 |

* By Pauling

In order to deduce the calculated values for $\Delta H$ wet by Eq. 3, it is necessary to calculate the appropirate values for $\Delta H_{\mathrm{D}}$. For this purpose, the following assumptions were made. (1). The negative charge on a sulfonic acid group exists on the position of the oxygen atom which is the immediate neighbor of the adsorbed cation, thus as the "ionic radius of sulfonic acid group," the van der Waals radius or the ionic radius of oxygen, which both happened to have the same value, 1.40 Å[8], was taken. (2.). The dry state of resin except hydrogen form is assumed to be similar to an ionic crystal, that is, the adsorbed ion and radical anion are coupled as ions also at the dry state, but because the pairs are distributed amorphously, the electrostatic interaction is almost limited to the coupled ions, thus the Madelung constant can be assumed to be unity. (3). Thus the electrostatic attraction by the Coulomb force of ion pairs can be expressed by

$$\Delta U = \frac{Ne^2 z'}{(r_i+1.40)} \times 10^8$$

c.g.s. e.s.u. per Eq.,......(6)

where $N$, $e$, and $r_i$ are as described above; $z'$, a corrected valency of ion considering the repulsion of the ions of same charge, is 1 for monovalent adsorbed ions, 1.75 for divalent ions, and it depends on ionic radius for trivalent ion (2.44 for aluminium). (4). $\Delta H_{\mathrm{D}}$, the energy required to separate the ion pairs infinitely, so to speak the "crystal energy of ion-exchange resin," is estimated roughly as much as about ninety percent of the electrostatic attraction $\Delta U$, considering the existence of the repulsion term. This figure was taken from the average value of several species of mono-monovalent ionic crystal[9]. (5). For

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[7] K. Fajans, *Naturwissenschaften*, **9**, 729 (1921).

[8] L. Pauling, "The Nature of the Chemical Bond," p. 189, 346 (1939).

[9] E. A. Moelwyn-Hughs, "Physical Chemistry," p. 599, (1940).

hydrogen form, we adopt a different model; that is, the atoms in the dry state of that form are no longer ionized but exist as covalent bond, and

$$\varDelta H_D = D + I - E, \qquad \ldots\ldots(7)$$

where $D$ is energy required to separate the covalent bond between the hydrogen atom and residual sulfonic radical, and $I-E$ is the difference between the ionization energy of hydrogen atom and the electron affinity of the sulfonic radical. As the value for $D$, 110 kcal. per mole, the covalent bond energy of O−H bond in water molecule, was conventionally used. The value for $I$ is 313 cal.; and for $E$, 88 kcal., the value of electron affinity of oxygen atom, was conventionally used.

Thus the calculated $\varDelta H_{\mathrm{WET}}$ is shown in column 7, Table II. The fair agreement between $\varDelta H_{\mathrm{WET}}$ observed and calculated, considering the fact that it is derived as the difference of the two large values, suggests that these assumptions just made are not going too far except in some cases. At the hydrogen form, where the deviation is very large, it is necessary to use more refined values for D and E. For divalent and trivalent cation forms, both the uncertainty in $\varDelta H_{\mathrm{HYD}}$ and the probable deviation from the above mentioned factor (90%) are enough to explain the poor coincidence between theory and experiment.

### Summary and acknowledgment

(1) The measurement of heats of wetting of strongly acidic and weakly acidic cation exchange resins and strongly basic anion exchange resins was made by a simple method and their great dependence on the adsorbed ion species was found.

(2) The series of heat of wetting with ion forms is almost parallel with the lyotropic series of ions, thus it has been shown that this penomenon has an important relation to the hydration of the ions. The acid form of the weakly acidic resin occupies a special position, and this is attributed to the undissociative nature of carboxylic radical.

(3) The result on the partially wetted samples supports the view that only a few water molecules which may be called "bound water" take part in the heat of wetting or hydration of ions.

(4) A theoretical interpretation based on a few assumptions was attempted and a fair agreement with the experimental results was obtained.

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*Rikkyo University*