Studies on the Heat of Solution. I. Heats of Solution of Crystalline Pentaerythritol and Mesoerythritol

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Introduction

The measurement of heat of solution of crystalline materials is one of the useful methods for the determination of heat of formation of solid solution as well as of molecular compound, energy content of meta-stable modifications, energy of lattice imperfections, etc. Since we have hitherto investigated the interaction energies of different kinds of molecules constituting crystalline molecular compounds by the method of vapor pressure measurement(1) and also the interaction of water and other materials by differential thermal analysis and other methods(2), we have undertaken to study the heat of solution of crystalline materials in these connections.

As is well known, among the substances interacting with water, a group of alcohols exhibits strong hydrogen bond with water. Although the measurements of the heat of solution as well as the heat of dilution of the univalent alcohols, and some saccharides have been made, accurate determinations for polyvalent alcohols are very scanty. Now that the crystal structure as well as the thermal properties of pentaerythritol(3)(4) and mesoerythritol(5) have been studied in considerable detail in our laboratory, we measured the heats of solution of these materials as the first step to the investigation on the heat of solution of crystals.

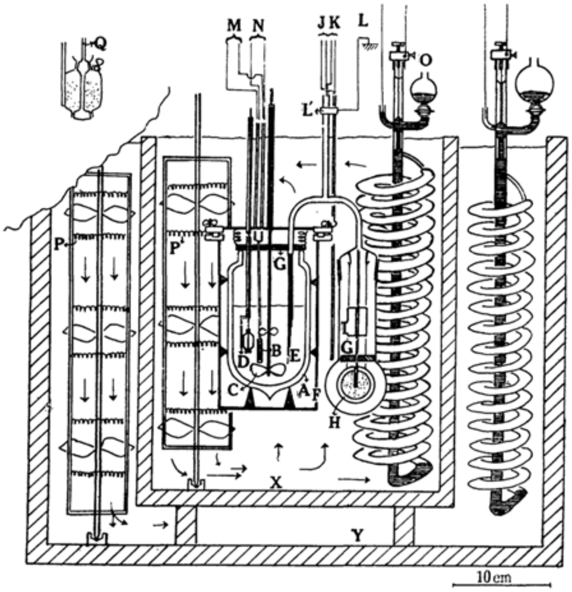

Fig. 1.

G: cork plate
I: lead block to avoid thermal leakage
J: main thermel measuring the temperature difference between calorimeter and fluctuation damper
K: thermocouple measuring the temperature difference between fluctuation damper and inner water jacket
L: earth to avoid leakage current
M: to voltmeter
N: to ammeter and battery
P: nichrome heater and stirrer

Experimental

(i) Apparatus and procedure: The calorimeter used is illustrated in Fig. 1. The calorimeter vessel consists of a silvered Dewar vessel (A) with a capacity of ca. 700 cc., containing the calorimeter heater (B), the glass stirrer (C), the dissolving device (D) for specimen under investigation and the junction points (E) of copper-constantan multiple thermocouple measuring the temperature variation of the calorimeter with reference to the average temperature of the inner water jacket (X). The Dewar vessel was mounted in a water-tight submarine jacket (F) which is made of 1 mm. thick copper sheet plated with chromium and polished on the surface. The air gap between the calorimeter vessel and the wall

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(1) I. Nitta, S. Seki, H. Chihara and K. Suzuki, *Sci. Paper Osaka Univ.*, No. 29 (1951); I. Nitta, S. Seki and H. Chihara, *J. Chem. Soc. Japan*, **70**, 387 (1949).

(2) I. Nitta and S. Seki, *J. Chem. Soc. Japan* **69**, 87 (1948); H. Chihara and S. Seki, This Bulletin, **26**, 88.

(3) I. Nitta and T. Watanabé, *Nature*, **140**, 365 (1937); I. Nitta and T. Watanabé, *Sci. Paper Inst. Phys. Chem. Research*, **34**, 1669 (1938); See also F. J. Llewellyn, F. G. Cox and T. H. Goodwin, *J. Chem. Soc.*, 883 (1937).

(4) a) I. Nitta, S. Seki and K. Suzuki, This Bulletin, **24**, 63 (1951); b) I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**, No. 9, 26 (1950); c) I. Nitta, S. Seki, M. Momotani, K. Suzuki and S. Nakagawa, ibid, No. 10, 11 (1950); d) I. Nitta, T. Watanabe, S. Seki and M. Momotani, ibid. No. 10, 19 (1950).

(5) I. Nitta, T. Watanabé and Y. Tomomatsu (unpublished).

of the submarine jacket was about 1.5 cm. The heat conductivity constant between the calorimeter and the outer part was found to be 0.8 cal./min. deg.

The temperature fluctuation of the outer water jacket (Y) (ca. 40 litres) was controlled within the accuracy of ±0.002°C., while the inner water jacket within ±0.0003°C. A sensitive toluene-mercury regulator (O), efficient stirring device (P) (the circulation of whole water is accomplished in the period of 5∼8 sec.), and a special electrical circuit for protection of oxidation of the mercury surface of the regulator were employed.

The temperature variation of the calorimeter was measured by means of twelve-junctions copper-constantan thermocouple, each junction of which was insulated with polystyrene and covered with thin glass capillary tubes separately. The standard reference junction points were introduced in the Swietoslawsky-type fluctuation damper(6) (H) made of copper sphere covered with a layer of paraffin (ca. 4 mm.) and a thin alminium foil, and the damper was immersed in the inner water jacket. With these constructions the temperature fluctuation of the standard reference junction was minimized to ±0.0001°C. The e. m. f. of the thermo-couple was measured by means of the "P-7 Type Low-voltage Potentiometer" (0.01μV.) of Yokogawa Electric Work in combination with the "RC Type Reflection Galvanometer" (0.2 μV./mm.) of Shimadzu Co. as null indicator. Special precautions were taken to exclude "vagabond e. m. f." caused in the circuit(7). Thus we could measure the temperature variation of 0.0001°C.

The water equivalent of the calorimeter was determined by electric energy. The heater for this purpose is made of constantan wire (ca. 10 ohm) wound on thin mica strips and insulated with a thin layer of polystyrene. The ampere and the voltage drop were measured by precision type ammeter and voltmeter. The source of constant current is a heavy duty lead storage battery (120 A. H.), which is controlled to a steady state by discharge into the ballast resistor of approximately the same resistance as the heater for a period of an hour or more before use.

The stirrer was operated with steady speed D. C. motor. The stirring velocity was regulated at about 170 r. p. m. and the heat produced by stirring at this velocity was about 0.23 cal./min. The dissolving device made of hard glass has a capacity 5∼10 cc. To dissolve the powdered specimen, the glass rod (Q) is pushed downward. The endothermic heat effect due to this operation, which may be ascribed to evaporation of water into the air bubbles escaping from the glass bulb, is found to be only about 0.3 cal. even for the largest vessel.

In every run, before the measurements, the calorimeter was immersed in the thermostat for about 3∼5 hours after the temperature of thermostat reached the stationary value. For the determination of the heat quantity from the temperature-time curve, the correction of heat exchange between the calorimeter and the water jacket was made by use of Newton's heat flow equation, and the other corrections mentioned above were also taken into consideration.

In order to test the usefulness of the calorimeter, the heat of solution of NaCl was determined (see Table 1). The result obtained coincides within the accuracy of 0.7% with the most reliable values at the same conditions recommended by Bichowsky and Rossini.(8)

Table 1

t°C.	Substance	N	ΔH_{soln} (this research) kcal./mol.	ΔH_{soln} (others) kcal./mol.
18	NaCl	400	1.218	1.225±0.005
18	Pentaerythritol	4300	4.77	
		2200	4.78	
		1100	4.79	6.3(9)
		620	4.83	
18	Mesoerythritol	4600	5.24	5.54(10)

(ii) Materials;

(a) NaCl: The product of "for analysis" of Takeda Co. was desiccated by heating for about five hours under high vacuum (10^{-4} mm. Hg or less) at about 150°C.

(b) Pentaerythritol: The product of Shionogi Co. was recrystallized from aqueous solution four times and then subjected twice to fractional sublimation at about 180°C. under high vacuum (m. p. 264°C.).

(c) Mesoerythritol: The product of Kahlbaum Co. was purified by fractional sublimation under high vacuum at about 110°C. (m. p. 120.3°C.). The crystal exists in two modifications, stable and metastable, at room temperature. The present specimen is of stable form.

(iii) Experimental Results: The results obtained are all given in Table 1 together with some other reference data. In this table N in the third column is the mole number of water to dissolve one mole of solute and the sign of enthalpy is taken positive for endothermic process. Comparing our values with the data in the fifth column, obtained at higher concentrations by other investigators, it is evident that the heats of dilution for both substances are a little exothermic. It is also observed that the heat of solution of pentaerythritol becomes almost constant when the degree of dilution exceeds N=1000.

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(6) W. Swietoslawsky, "Microcalorimetry", Reinhold Publishing Co., 1946.

(7) "Temperature, its Measurement and Control in Science and Industry", Reinhold Publishing Co., 1944, p. 265.

(8) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances", Reinhold Publishing Co., 1936.

(9) From temperature dependence of solubility (22∼58°C, N=47∼22) Cooke, *Paint. Manif.*, **18**, 125 (1948).

(10) M. Berthelot, *Ann. Chim. et Phys.* **26**, 201 (1892) (24°C, N=300).

Table 2

Substances	$-\Delta H^{\infty}_{\text{soln}}$ (or $\Delta H^{\infty}_{\text{mix}}$)	ΔH_{subl} (or ΔH_{vap})	$-\Delta H^{\infty}_{\text{hyd}}$ (obs)	$-\Delta H^{\infty}_{\text{hyd}}$ calc. from (2) & (3)	$-\Delta H^{\infty}_{\text{hyd}}$ calc. from (5) & (6)
Ethylene Glycol	(1.7)	(14.9)	16.6	20.9	18.5
Glycerol	(1.5)	(20.0)	21.5	30.6	25.9
Mesoerythritol	−5.2	32.3 (22.3)	27.1	41.4	34.5
Pentaerythritol	−4.8	31.4 (19.2)	26.6	40.3	33.6

Discussion of Results

As mentioned above, the heats of dilution of both substances are exothermic. Recently, Lange and his coworkers(11) measured the heats of dilution of univalent alcohols, and saccharides, and found that they are exothermic similarly to what we found in the present experiment. They explained this exothermic effect to be ascribed to the dissociation of the associated solute molecules. Even though we have not obtained the data of heats of dilution accurately enough to permit us to draw a definite conclusion on the mechanisms of the dissociation of hydrogen bond of polyalcohols investigated, it seems very plausible to assume that the exothermic heats of dilution of the present materials would also be due to the dissociation of the dimer or higher associates.

Now, we should like to discuss further the hydration state of the polyalcohols. As is well known, the heat of hydration is given by the following relation:

$$\Delta H^{\infty}_{\text{hyd}} = \Delta H^{\infty}_{\text{soln}} - \Delta H_{\text{subl}}, \tag{1}$$

where $\Delta H^{\infty}_{\text{hyd}}$ indicates the heat of hydration at infinite dilution, ΔH_{subl} the heat of sublimation and $\Delta H^{\infty}_{\text{soln}}$ the heat of solution of crystal to form infinitely dilute aqueous solution. If the substance to be dissolved is liquid, the heat of vaporization and heat of mixing take the places of heats of sublimation and of solution, respectively. In Table 2 we give $\Delta H^{\infty}_{\text{soln}}$ (or $\Delta H^{\infty}_{\text{mix}}$), ΔH_{subl} (or ΔH_{vap}) and $-\Delta H^{\infty}_{\text{hyd}}$ of the substances investigated and of other related ones. The heats of solution listed in Table 1 may be regarded approximately as $\Delta H^{\infty}_{\text{soln}}$ on account of the independence on the concentration as shown in the column 4. As to the heats of sublimation we have already reported.(5a)(5c) The heats of mixing at infinite dilution of ethylene glycol(12) and glycerol(13) are estimated from the extrapolation of the data at higher concentrations to the infinite dilution. For the heat of vaporization of ethylene glycol, the data by Louguinine(14) at 90°C was adopted. For glycerol there is reported the temperature variation of vapor pressures by Stedman.(15) The calculated heat of vaporization from them (21.17 kcal./mole at 75°C), however, seems to be not so trustworthy on accont of the unreasonably large value in comparison with that of pentaerythritol (19.2 kcal./mole) and of mesoerythritol (22.3 kcal./mole), having four hydroxyl groups, and of abnormally high dependence of the heat of vaporization on the temperature. So, we estimated 20 kcal./mole for the heat of vaporization of glycerol (See Table 2).

According to Butler,(16) the heats of hydration of univalent alcohols may be calculated by the following semi-empirical equations (2) and (3),

$$\Delta H^{\infty}_{\text{hyd}} = \left\{ \frac{n}{2}\gamma_{\text{W-W}} - n_{\text{W-CH}}\gamma_{\text{W-CH}} - n_{\text{W-OH}}\gamma_{\text{W-OH}} \right\}, \tag{2}$$

$$n = n_{\text{W-CH}} + n_{\text{W-OH}}, \tag{3}$$

where n is the total number of water molecules hydrated to the solute molecule in question, $n_{\text{W-CH}}$ and $n_{\text{W-OH}}$ the number of hydrated water molecules for CH and OH groups respectively; $\gamma_{\text{W-W}}$ is the energy required to separate a single pair of water molecules, and $\gamma_{\text{W-CH}}$, $\gamma_{\text{W-OH}}$ the energies of interaction between a hydrated water and a CH or OH group, respectively. Putting somewhat artificial assumptions of

$$\gamma_{\text{W-W}} = 5.25,\ \gamma_{\text{W-CH}_3} = 3.4,\ \gamma_{\text{W-CH}_2} = 3.4,$$
$$\gamma_{\text{W-CH}} = 3.4 \text{ and } \gamma_{\text{W-OH}} = 5.6, \tag{4}$$

for the interaction energies (in kcal./mole), and $n_{\text{CH}_3} = 3$, $n_{\text{CH}_2} = 2$, $n_{\text{CH}} = 1$ and $n_{\text{OH}} = 3$ for the number of hydrated water molecules, Butler found that the calculated $\Delta H^{\infty}_{\text{hyd}}$ values from the above equations are in good agreement with the observed values for normal univalent alcohols, and also that they are always larger by 0.8 kcal. per one branching than the observed data for branched alcohols. We have tentatively calculated the heats of hydration of polyvalent alcohols with application of these values and found indeed large positive deviations as shown in the fifth column in Table 2.

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(11) E. Lange and H. G. Marlcgraf, *Z. Electrochem.*, **54**, 73 (1950).

(12) a) International Critical Table. (average value of following two: Berthelot, (1882); de Forcrande, (1890).); b) F. Schwers, *Z. phys. Chem.*, **75**, 366 (1911).

(13) a) I. C. T. average value of Berthelot (1873, 1976), de Forcrande (1887, 1888), Gerlach (1884) and Kolossowsky (1913); b) Katz. *Proc. Amsterd. Acad.*, **13** 970 (1911) R. Fricke and J. Lücke, *Z. Electrochcm.*, **35**, 636 (1929).

(14) W. Louguinine, *Ann. chim. et phys.* **26** 239 (1902); W. Hieber and A. Waeruer, *Z. Electrochcm.*, **40**, 252 (1934).

(15) D. F. Stedman, *Trans. Faraday Soc.*, **24**, 296 (1929).

(16) J. A. V. Butler, *Trans. Faraday Soc.*, **32**, 229 (1936).

Table 3

Substances	Molecular Volume	n	n'	θ'	θ'/θ_0	$q=\theta'/\theta$
Ethylene Glycol	55.6[a]	10	8.18	9.8	1.67	0.83
Glycerol	72.8[a]	14	10.08	13.1	2.28	0.73
Mesoerythritol	92.0[b]	18	12.22	16.9	2.90	0.71
Pentaerythritol	110.0[c]	20	14.22	16.2	2.77	0.69

a: Taken from reference⁽¹⁸⁾.

b: We estimated the density of liquid from that of solid, assuming volume change on fusion is 10%.

c: As the present material belongs to the so-called plastic crystal (see reference⁽²¹⁾), we estimated the density of liquid from those of the two modification of solid, and heats of fusion and transition⁽⁴⁾, using following relation:

$$\frac{\Delta V(\text{fusion})}{\Delta V(\text{transition})}=\frac{\Delta H(\text{fusion})}{\Delta H(\text{transition})}$$

To elucidate the nature of this deviation we have attempted to calculate $\Delta H^{\infty}_{\rm hyd}$ of the polyvalent alcohols employing the experimental values of $\Delta H^{\infty}_{\rm hyd}$ of a series of univalent alcohols and an other equation of some different meanings from that of Butler, instead of adopting somewhat artificial choice of n and γ values given above.

Supposing that the hydrated water molecules are not permanently fixed to the solute molecules owing to the thermal agitation, then the number n may be considered to have only a statistical meaning.⁽¹⁷⁾ Accordingly this number may not necessarily be an integer as Butler has assumed. To create a cavity to hold a solute molecule in the liquid, the number of hydrogen bonds to be broken (n') will be 4, 6, 8, 10 and 12, if the volume of a cavity is 1, 2, 3, 4 and 5 integral multiples of that of a water molecule. It is possible, then, to determine the number n' from the ratio of the molecular volume of solute to that of water, using interpolation of above-mentioned relations between n' and molecular volume ratio. The numbers n' obtained in this way are given in Tables 3 and 4. (n' differs from n, and the relations to the heats of hydration of univalent alcohols are given in Fig. 2.) Then, inserting equation (3) into (2) and taking into account the effect of branching, we have

$$\begin{aligned}\Delta H^{\infty}_{\rm hyd} &= n'\left\{\frac{1}{2}\gamma_{\rm W-W}-\gamma_{\rm CH-W}\right\}\\ &\quad -n_{\rm W-OH}\{\gamma_{\rm W-OH}-\gamma_{\rm W-CH}\}\\ &\quad +\{\text{effect of branching}\}\\ &=n'\varphi-\theta+\delta \qquad (5)\end{aligned}$$

In this equation integral number n in (2) is replaced by n', and θ is proportional to the number of OH groups in the solute molecule if the intramolecular interaction between OH groups is negligibly small.

Table 4

Substances		$n^{(16)}$	$n'^{(18)}$	$-\Delta H^{\infty}_{\rm hyd}$ (obs.)
Methyl	Alcohol	6	6.50	11.24
Ethyl	〃	8	8.46	12.88
Propyl-	〃	10	10.28	14.42
Butyl-	〃	12	12.14	15.94
Amyl-	〃	14	14.06	17.50
Iso propyl-	〃	10	10.46	13.45
Iso butyl-	〃	12	12.24	15.24
sec-Butyl-	〃	12	12.18	15.06
tert-Butyl-	〃	12	12.42	14.44
tert-Amyl-	〃	14	14.06	15.69

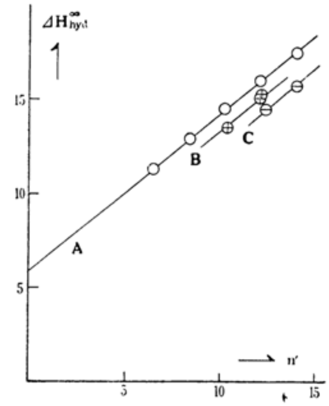

Fig. 2.

A: normal alcohols
B: one branched alcohols
C: two branched alcohols

As shown in Fig. 2 experimental data of normal, one-branched, two-branched univalent alcohols lie on three different straight lines. Thus, from these lines and equation (5), we obtain the following relations:

$$\varphi_0=-0.834,\quad \theta_0=5.82 \text{ and } \delta_0=0.80/\text{branch}. \qquad (6)$$

(suffix $_0$ means the value of univalent alcohol)

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(17) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6** 666 (1941); J. A. Pople, *Proc. Roy. Soc.*, A **205**, 163 (1951).

(18) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds", Elsevier Publishing Co., 1950.

The reason for the appearance of the correction factor δ may be explained by the following; (i) as was pointed out by the present authors,(4a) the polarizabilities of the carbon atoms in branched hydrocarbons are somewhat smaller than that of the normal one, so the contributions of the dispersion and induction interaction energies become smaller; ii) in branched hydrocarbons the interatomic distances between hydrated water molecules and the inner carbon atoms are larger than that of the normal one, hence, the contribution to the interaction energy of these atoms becomes smaller.

Inserting n' values derived from the molecular volume of solute in liquid state into equation (5) under the assumption that the intramolecular interaction of OH groups is negligible and putting in the numerical values of equation (6), we obtain the heats of hydration of polyvalent alcohols given in the last column in Table 2. There remain still some deviations from the experimental values, although they are diminished considerably in comparison with the results obtained by the method of Butler. Certainly, the origin of these deviations is to be attributed to the intramolecular interaction of OH groups which gives rise to decrease of the number of hydration water molecules. The similar fact has been recently observed by Shimura.(19) He measured the electrostriction of water caused by dissolving various sorts of amino acids and found that, in comparison with the δ- or γ-amino acid the electrostriction caused by NH_3^+ group of α-amino acid is decreased. As a measure of decrement of intermolecular hydrogen bond forming powers of OH groups in the polyvalent alcohols, we have tentatively calculated the factor $q=\theta'/\theta$. Here θ' is given by use of equation (5) from the observed heat of hydration of polyvalent alcohol and the values of φ and δ of the univalent alcohols. The results are given in the last column of Table 3 which indicate evidently the intermolecular interactions decrease (intramolecular interaction increases) from ethylene glycol to pentaerythritol. As to the former, it has been found recently(20) that from the study of infra-red spectroscopy intramolecular hydrogen bond of this molecule in solution state is not so strong as expected before. On the other hand, the possibility of more frequent formation of the intramolecular hydrogen bond may be enhanced by the internal rotation about C-C single bond in the case of more complex polyvalent alcohols. This may, in part at least, explain the decreasing tendency of q-values given in Table 3.

Summary

(i) The heats of solution of pentaerythritol and mesoerythritol have been measured at 18°C and found to be both of endothermic. (4.77 kcal./mole and 5.24 kcal./mole).

(ii) The heats of dilution of both substances are of exothermic.

(iii) From the heats of sublimation and of solution, the heats of hydration were determined (26.6 kcal./mole for pentaerythritol and 27.1 kcal./mole for mesoerythritol).

(iv) It was found that the intramolecular hydrogen bonds cause considerable deviations from the improved Butler rule on the heats of hydration of alcohols.

In conclusion the authors wish to express their sincere thanks to Professor Nitta for his kind guidance throughout this work. The cost of this investigation was defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Expenditure Grant from the Ministry of Education to which the authors' thanks are due.

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(19) K. Shimura, *J. Agr. Chem. Soc. Japan*, **23** 31, 48 (1949); **24** 412 (1951).

20) R. Mecke, *Z. Electrochem.*, **52**, 269 (1948).

(21) S. Seki, *J. Chem. Phys.*, **18**, 397 (1950).