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EMPIRICAL CONSIDERATIONS OF ENTROPY III. A STRUCTURAL APPROACH TO THE ENTROPIES OF AQUEOUS ORGANIC SOLUTES AND COMPLEX IONS

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February 3, 1953

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EMPIRICAL CONSIDERATIONS OF ENTROPY

III. A STRUCTURAL APPROACH TO THE ENTROPIES  
OF AQUEOUS ORGANIC SOLUTES AND COMPLEX IONS\*

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Department of Chemistry and Chemical Engineering  
University of California, Berkeley, California

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ABSTRACT

A method for estimating the entropy of complex aqueous organic solutes and related species has been developed by a structural extension of a method of Powell and Latimer for simple solutes. The agreement between calculated and observed values is, in general, good, although systematic deviations begin to occur for very complicated and large solutes. The method is extended to the calculation of the entropies of charged organo-metallic complex ions with good success, and possible applications to systems of biological interest are indicated.

Subsequent to the development of the general method for estimating the entropies of aqueous solutes, an empirical equation is also given for calculating gaseous entropies of both inorganic (ionic) and organic molecules from their structures.

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\*This work was performed under the auspices of the AEC.

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INTRODUCTION

The success of our previous attempts, as well as others,<sup>1,2</sup> to correlate and calculate the entropies of aqueous inorganic ions<sup>3</sup> has led to an investigation of a similar correlation for organic aqueous species. These molecules are of particular interest due to current interest in organic complexing and chelating agents<sup>4</sup> and are much more general and abundant and varied than inorganic species. Further, the accumulation of the thermodynamic data for many types of organic compounds<sup>5</sup> has now provided a sizeable amount of information with which (when combined with suitable solubility determinations) one can evaluate the absolute entropies for aqueous complexing agents. In some

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\*This work was performed under the auspices of the AEC.

<sup>1</sup>R. E. Powell and W. L. Latimer, J. Chem. Phys. 19, 1139 (1951).

<sup>2</sup>R. E. Powell and R. E. Connick, Private Communication, 1952.

<sup>3</sup>J. W. Cobble, J. Chem. Phys., in press; papers I and II of this sequence.

<sup>4</sup>A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, 1952.

<sup>5</sup>Summarized in Volumes I-III, "Annual Review of Physical Chemistry," Annual Review, Stanford, California, 1950-52.

cases of neutral solutes, the activity coefficients and thermochemical heats of solution are also available so that as a class the data for neutral organic species are as accurate as that available for inorganic solutes.

An attempt is also made to correlate the data available for metallo-organic complexes and chelates, although the data for this particular species are probably the least accurate yet treated. Nevertheless, we can semiquantitatively illustrate some general principles which are believed will be generally applicable and useful.

#### STRUCTURAL DEPENDENCE

One can conclude from the previous treatments that the size of an aqueous solute is primarily responsible for the magnitude and sign of its partial molal entropy. While the charge is also important, this is probably due to the effect of orientation of nearby water molecules, which can be looked upon as a change in the effective size of the solute. In the inorganic ions, the size of an ion could be related to rather well-defined interatomic distances in the ion. This method proved successful probably because of the inherent simplicity and limited number of atoms in the inorganic ions. Further, those ions of larger size (i.e., complex ions) usually possessed high symmetry ( $\text{PtCl}_6^{-2}$ ,  $\text{Fe}(\text{CN})_4^{-4}$ ) and could also be well defined by a single interatomic distance. With organic ions, the simplicity and symmetry rapidly disappears with increasing numbers of atoms, and it was clear that some other method would have to be used for organic solutes. One perhaps could effectively use the partial molal volumes, but these data are not generally available. A possible solution can be found in the

recent treatment that Powell and Latimer<sup>1</sup> have proposed, which bases the aqueous entropy upon the molar volume of the pure liquid state of the solute. The equation which they give is:

$$\bar{S}^{\circ} = 10 + \frac{3}{2} R \ln M + S_{(\text{int.})} - 0.22 V_m \quad (1)$$

where  $\bar{S}^{\circ}$  is the partial molal entropy at 25<sup>o</sup> for the hypothetical one molal ideal solution of a solute of mass M which has a molar volume,  $V_m$ , in the pure liquid state at 25<sup>o</sup> C.  $S_{(\text{int.})}$  is the internal entropy of the molecule, which is assumed to be the same for the dissolved solute as for that of the gaseous molecule, and is thus given by the total entropy,  $S_{(g)}^{\circ}$ , less the translational entropy,  $3/2 R \ln M + 26.00$ . The gaseous entropy,  $S_{(g)}^{\circ}$ , can be approximated by the entropy of the pure substance plus its entropy of vaporization, but the entropy of vaporization is not always available for substances which are solids at ordinary temperatures, or which decompose easily when heated (sugars, amino-acids, etc.). Therefore, use has been made of the observations previously made by others that the entropies of pure organic compounds are generally additive in some simple manner depending upon the number of atoms in the molecule, and in the way in which it is put together.<sup>6-8</sup> Theoretical justifications for these empirical

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<sup>6</sup>G. S. Parks and H. M. Huffman, "The Free Energies of Some Carbon Compounds," Chem. Catalogue Co., New York, 1932.

<sup>7</sup>H. M. Huffman and E. L. Ellis, J. Am. Chem. Soc. 57, 46 (1935); 59, 2150 (1937).

<sup>8</sup>National Bureau of Standards and American Petroleum Institute Circular C-461, "Selected Values of Properties of Hydrocarbons," Washington, D.C., 1947.



treatments have been discussed by others.<sup>9,10</sup> An equation which will reproduce the entropies of gaseous molecules (standard state: ideal gas at unit fugacity, 25° C.) has been found by inspection of the entropies for a wide variety of compounds:

$$\begin{aligned}
 S_{(g)}^{\circ} &= S_{(\text{Trans.})}^{\circ} + 9.2 (N) - S_{(s)}^{\circ} \\
 &= \frac{3}{2} R \ln M + 26.00 + 9.2 (N) - S_{(s)}^{\circ}, \quad (2)
 \end{aligned}$$

where N represents the number of "skeletal" bonded atoms in the compound (total bonded atoms minus hydrogens), M is the mass of the molecule, and  $S_{(s)}^{\circ}$  is the entropy loss computed empirically from the observation that double bonds, rings, and branched chains all lower the entropy from an equivalent "normal" linear molecule. The entropy-loss values are given in Table 1. It seems to make little difference whether N is an nitrogen, sulfur, hydrogen, or oxygen atom instead of carbon, and equation (2) will, for N = 0, reduce to that required for monatomic gases. Electronic contributions to the ground states of atoms and molecules have been ignored.

Table 1

Structural Correction Entropy Values	
Structure	$-S_{(s)}^{\circ}$ (e.u.)
double-bond	3.5
triple-bond	4.5
ring	14
branched chain	3.0
> 3 Adjacent -OH groups	16

<sup>9</sup>M. L. Huggins, J. Chem. Phys. 8, 181 (1940).

<sup>10</sup>K. S. Pitzer, Chem. Rev. 27, 39 (1940).

The origin of the required subtraction of 16 e.u. for molecules possessing  $\geq 3$  neighboring -OH groups is interesting. It was first noticed by inspection of the solution data and thought to be due to some special type of interaction of the solute molecule with the solvent. Actually, however, it can be demonstrated that the effect is also present in the gaseous molecule, and therefore probably does not constitute a bona-fide deviation from equation (1). Thus, the calculated value for the entropy of gaseous glycerin without the correction is 92 e.u. and with it, 76 e.u. The observed value (calculated from vapor pressure measurements and the entropy of liquid glycerin) is 80 e.u.

The empirical constants given are based upon the following general considerations: a) A cyclic ring in a compound is treated as a single atom when computing branched chains, thus methyl benzene and dimethyl benzenes would be considered as having no branched chains, while trimethyl benzene would have one; b) a branched (but not terminal)  $\text{NH}_2$  group is ignored in computing "N" and  $S^\circ(\text{s})$ , but not in "M", the molecular weight (this effect has long been observed by others, and we have also invoked this special exception); c) the number of double and triple bonds in related compounds are determined by classical structures:  $\text{O} = \text{C} = \text{S}$ ,  $\text{N} \equiv \text{N} = \text{O}$ ,  $\text{CH}_3 - \text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$ . The justification for all of these "rules" is purely empirical. One could, of course, formulate so many rules that while the entropies could then be exactly calculated to a high precision, the method would soon lose its generality and usefulness. With the above few generalizations, all of the known gaseous entropies have been reproduced to an average

deviation of a few entropy units.<sup>11</sup>

Combining equations (1) and (2) the following expression is obtained:

$$\bar{S}^{\circ} = 10 + \frac{3}{2} R \ln M + 9.2 (N) - S_{(s)}^{\circ} - 0.22 V_m. \quad (3)$$

This equation is a structural extension of equation (1), but generally more useful in the above form since the entropies for many species can now be calculated for which no detailed information is available on the gaseous state. A test for equation (3) is afforded by Table 2 in which the observed and calculated partial molal entropies for a wide variety of species have been summarized. The average deviation is about 3 e.u., the largest uncertainty frequently resulting from the necessity of approximating the molar volume, but this can usually be done for simple molecules by the parachor method, by estimation from the solid (by decreasing the density of the solid by ~10 percent), or from the densities of concentrated solutions. Fortunately, the low coefficient, 0.22, removes the necessity for knowing  $V_m$  very accurately, although some exceptions to this generalization will be found in a later section

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<sup>11</sup>It should be pointed out that the applicability of equation (2) is not limited to organic molecules. Thus, we compare the observed and calculated values for the gaseous entropies at 25° for a wide variety of inorganic compounds:  $BBr_3$ : 77.49, 77;  $KCl$ : 57.2, 57;  $IBr$ : 61.8, 60;  $OsO_4$ : 65.6, 69;  $GeO$ : 52.6, 54;  $B_3N_3H_3$ : 73.7, 80;  $Re_2O_7$ : 100, 94;  $SO_3$ : 61.24, 62;  $CO$ : 47.3, 51.

on metallo-organic ions.

Table 2

Comparison of Calculated and Observed Aqueous  
Partial Molal Entropies at 25° C

$\Delta S^\circ$ refer- ence	Species	$S_{25}^\circ$ (a)	$\Delta S^\circ$ (b)	$S_{(obs.)}^\circ$ (b)	$S_{cal.}^\circ$	$\Delta$ (c)
12	He(g)	30.13	-18.5	11.6	12	0
12	Rn(g)	42.10	-26.3	15.8	16	0
13	HF(g)	41.47	-15.5	<u>26</u>	24	2
13	H <sub>2</sub> S(g)	49.15	-20.0	29.2	23	6
13	NH <sub>3</sub> (g)	46.01	-19.7	26.3	24	2
12, 14	CH <sub>4</sub> (g)	44.50	-23.8	23.5	21	3
12	C <sub>2</sub> H <sub>2</sub> (g)	47.997	-17.6	30.4	28	2
12	C <sub>2</sub> H <sub>4</sub> (g)	52.45	-23.3	29.2	28	1
12, 14	C <sub>2</sub> H <sub>6</sub> (g)	54.85	-28.4	26.5	26	-1
12	CH <sub>3</sub> Cl(g)	55.97	-25.6	30.4	29	0
13	HCN(g)	48.23	-17.4	<u>30.8</u>	33	-2
12	CH <sub>3</sub> OH(g)	56.8	-27.0	31.6	30	2
12	NO(g)	50.339	-21.4	28.9	30	-1
12	O <sub>2</sub> (g)	49.003	-23.3	25.7	23	3
12	CO(g)	47.30	-21.8	25.5	29	-3
13	CO <sub>2</sub> (g)	51.061	-22.1	29.0	31	-2
13	SO <sub>2</sub> (g)	59.40	-21.4	<u>38</u>	36	2
15	CNI(g)	61.26	-23.4	37.9	37	1
13	HClO, aq.			<u>42</u>	37	5
13	HCOOH(l)	30.82	8.3	39.1	36	3

Table 2 (Continued)

$\Delta S^\circ$ refer- ence	Species	$S_{25}^\circ$ (a)	$\Delta S^\circ$ (b)	$\bar{S}^\circ$ (b) $\bar{S}_{(obs.)}$	$\bar{S}^\circ$ $\bar{S}_{cal.}$	$\Delta$ (c)
12	$C_2H_5OH(g)$	67.4	-32.8	34.6	36	-1
14	$C_3H_8(g)$	64.51	-32.0	32.5	32	0
12	$CO_2(g)$	55.34	-27.1	28.2	32	-4
13	$H_2N_2O_2, aq.$			<u>52</u>	50	2
15	$(NH_2)_2CO(c)$	25.00	16.6	41.6	42	0
14	$C_4H_{10}(g)$	74.10	-33.4	40.7	38	3
12	$(CH_3)_2CO(g)$	(16) 72.7	-27.1	45.6	43	3
12	$i-C_3H_7OH(g)$	(16) 78.3	-35.5	42.8	43	0
12	$CHCl_3(g)$	70.86	-35.8	35.1	40	-5
13	$CH_3COOH(l)$	38.2	4.8	43.0	39	-4
12	$n-C_4H_9OH(g)$	(17) 86.7	-44.0	42.7	49	-6
12	tert.- $C_4H_9OH(g)$	(17) 78.0	-39.6	38.4	42	-4
12	$CCl_4(g)$	73.95	-30	44	44	0
12	$(C_2H_5)_2O(g)$	(17) 83.3	-42.5	40.8	49	-7
18	$CH_2(NH_2)COOH(c)$	31.6	9.5	41.1	38	3
13	$H_3PO_4, aq.$			<u>42.1</u>	46	-4
12	$CH_3COOC_2H_5(g)$	85.6	-35.1	50.6	51	-1
19	glycerol(l)	49.7	-4.7	45.0	46	-1
20	$C_6H_6(l)$	41.30	-5.6	35.7	34	2
18	$p-C_6H_4Cl_2(c)$	41.9	4.4	46.3	49	-3
21	$CH_3C_6H_5(l)$	52.48	-8.1	44.4	43	1

Table 2 (Continued)

$\Delta S^\circ$ reference	Species	(a)	(b)	(b)	$\bar{S}_{\text{cal.}}^\circ$	$\Delta$ (c)
		$S_{25}^\circ$	$\Delta S^\circ$	$\bar{S}_{\text{(obs.)}}^\circ$		
21	$C_2H_5C_6H_5(l)$	60.99	-11.1	49.9	46	4
21	p-xylene(l)	59.12	-11.0	48.1	47	1
18	phenol(s)	34.0	8.6	42.6	42	1
18	d,l leucine(c)	<u>(7)49.5</u>	1.3	50.8	50	1
21	$C_6H_5COOH(c)$	40.8	5.95	46.8	49	2
20	naphthalene(c)	38.89	8.6	47.5	43	5
20	biphenyl(c)	49.2	4.8	54.0	52	2
18	l-sorbose(c)	<u>(22)52.8</u>	11	64	66	-2
18	mannitol(c)	57.0	18	75	77	-2
18	l-tyrosin(c)	<u>(7)53.0</u>	6.9	59.9	62	-2
18	l-cystine(l)	<u>(7)68.5</u>	-13.5	55.0	56	-1
18	Palmitic Acid(c)	113.7	-9	105	120	-15
19	Sucrose(c)	86.1	10.1	96.2	127	-31

(a) Values taken from references 7, 8, 13, and 15 unless otherwise indicated.

(b) Underlined values indicate that  $\bar{S}^\circ$  was calculated from sources other than the entropy of solution.

(c)  $\Delta \equiv \bar{S}_{\text{(obs.)}}^\circ - \bar{S}_{\text{(calc.)}}^\circ$ .

<sup>12</sup>J. A. V. Butler, Trans. Faraday Soc. 33, 229 (1937); Butler's standard state ( $N_2 = 1$ , and  $p = 1$  mm. Hg.) requires the subtraction of 21.2 e.u. to conform to the one used in this paper.

<sup>13</sup>W. L. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, New York (1952).

<sup>14</sup>W. F. Claussen and M. F. Polglase, J. Am. Chem. Soc. 74, 4817 (1952); corrected to our standard state by subtraction of 8.0 e.u.

<sup>15</sup>National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D.C., 1949.

<sup>16</sup>S. C. Schumann and J. G. Aston, J. Chem. Phys. 6, 480 (1938).

<sup>17</sup>Gaseous entropies estimated from entropies of liquids given in references indicated and vapor pressure data summarized in J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

<sup>18</sup> $\Delta S$  values estimated from solubility-temperature data given in A. Siedell, "Solubilities of Organic Compounds," Van Nostrand, New York, 3rd edition, 1941; supplement, 1952; for phenol and mannitol, heat of solution from I.C.T., Vol. 5, 1st ed., p. 150.

<sup>19</sup>Solubility and activity coefficient data from Scatchard, Hamer, and Wood, J. Am. Chem. Soc. 60, 3067 (1938); heat of solution data from I. C. T., Vol. 5, 1st ed., p. 150.

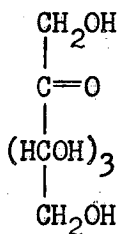
<sup>20</sup>R. L. Bohon and W. F. Claussen, J. Am. Chem. Soc. 73, 1571 (1951). These authors give  $\Delta S$  instead of  $\Delta S^\circ$  values and their data have been recalculated; the  $\Delta \bar{H}$  values from which  $\Delta S^\circ$  is calculated for naphthalene and diphenyl are given for the equilibria involving supercooled liquids and have been corrected to the stable crystalline reference state by the heats of fusion of these compounds and the specific heats given in Spaght, Thomas, and Parks, J. Phys. Chem. 36, 883 (1932).

<sup>21</sup>V. Jones and H. N. Parton, Trans. Faraday Soc. 48, 8 (1952).

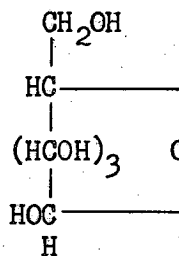
<sup>22</sup>G. W. Jack and G. Stegeman, J. Am. Chem. Soc. 63, 2121 (1941).

Since the deviations of palmitic acid ( $N = 18$ ) and sucrose ( $N = 23$ ) are both in the same direction, we would conclude that the proposed treatment becomes invalid for extremely large aqueous solutes. This deviation probably is due to the entropy of solution factors, or failure of the original Powell and Latimer equation (1), since our empirical equation for gaseous species agrees well with what experimental data are available for large gaseous molecules. If one plots the function  $\bar{S}^{\circ} - 3/2 R \ln M + S_{(s)}^{\circ}$  against " $N$ ", a smooth curve can be drawn through the values and is linear (in agreement with equation 3) below  $N \approx 14$ . With such a "working" curve, values can still be accurately estimated for large " $N$ " values even though our original expression is no longer valid.

It is of interest that poorer agreement is obtained between calculated and observed aqueous entropies if the cyclic structure of sugars had been ignored:



calc.: 76 e.u.

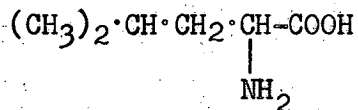


calc.: 66 e.u.

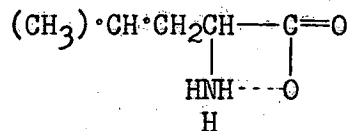
(*l*-Sorbosc: obs.: 64 e.u.)

The amino acids also present a special class of compounds, but are formally well represented in the present treatment by assuming the "zwitterion" is in effect a cyclic compound, by partial charge cancellation:





calc.: 64 e.u.



calc.: 50 e.u.

(d, l, leucine, obs.: 50.8 e.u.)

The contribution of the  $\text{NH}_2$  itself has, in accord with our previous "rules," been ignored. Conversely, the general applicability of the treatment may also be of help to identify the structure of the solute when its entropy is known.

It might be pointed out that a consequence of Powell and Latimer's original equation is that the entropy of solution of a gaseous solute is given by:

$$\Delta S^\circ = -(16 + 0.22 V_m). \quad (4)$$

This equation can then be used to test  $\Delta S$  data for which the absolute entropy of the solute is not available. In general, the agreement between calculated and experimental values is excellent except in the cases of solutes with large molar volumes which have somewhat larger- $\Delta S$  values than predicted.

#### IONIC ORGANIC SPECIES

The treatment given above can be extended to ionic species by differentiating equation (3):

$$d\bar{S}^\circ = 9.2 dN - dS_{(s)}^\circ - 0.22 dV_m + \frac{3}{2} R d \ln M \quad (5)$$

Thus, the entropy of some member of an ionic homologue can be calculated from another simpler member by adding the entropy required by equation (5) for their differences in structure, numbers of atoms, and molar volumes. For example, we calculate from acetate ion ( $\bar{S}^\circ = 20.8$  e.u.)

30 e.u. for benzoate ion (obs.: 27.9).<sup>11</sup> Formate ion was not used since it does not possess a "hydrocarbon" group, but from its entropy of 22.7 e.u., bicarbonate is calculated to be 26 e.u. (obs.: 22.7). The difference between  $\text{CNO}^-$  and  $\text{CNS}^-$  is calculated to be 2.9 e.u. (obs.: 2.7 e.u.). The entropy of malonate ion is estimated to be 17.6 e.u., from oxalate ion, 10.6 e.u., etc. When more data are available, this method can be tested more exactly for its general applicability. (See also reference 3.)

#### METALLO-ORGANIC IONS: COMPLEXES AND CHELATES

In a previous paper<sup>3</sup> it was demonstrated that the entropies of complex inorganic ions could be correlated when the "corrected" entropies ( $\bar{S}^1$ ) were considered:

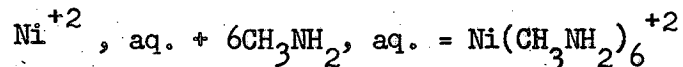
$$\bar{S}^1 = \bar{S}^0 - n(\text{H}_2\text{O}), \quad (6)$$

where  $n$  represents the number of water molecules replaced from the central ion on complexing, and  $\bar{S}^0$  is the partial molal entropy as normally used. It is with some assurance, therefore, that the same method can be applied to the organic ions, and these entropies can now be calculated in the following manner: As the simple ion is covered with organic ligands, the polar parts of the molecule will be oriented towards the central ion, so that the organic complex now presents a hydrocarbon "shell" to the solvent. The net effect is to screen or insulate the charge of the central ion, provided the organic ligand has a chain which is 2-3 atoms long. The entropy can be calculated by then assuming the complex is made up of hydrocarbon equivalent atoms by use of equation (2). This entropy is to be identified with  $\bar{S}^1$ ,  $\bar{S}^0$  being finally calculated by equation (6). It should be noted

that when organic molecules form chelates, two molecules of water per ligand are replaced, cyclic structures being formed in the process. Thus, "n" cannot be simply determined by the number of molecules in the complex ion, although usually values are reported for the maximum coordination, from which the structure (simple coordination or chelation) can then be inferred.

There are so few absolute entropies for organic complex ions available that it seems desirable to test the method proposed here by the entropy change data,  $\Delta S^\circ$ , which are more available.<sup>23</sup> There are two ways this can be done: calculate  $\Delta S^\circ$  from estimations of the entropies of both the ligand and complex species, or, estimate the entropy of the ligand and calculate  $\bar{S}^\circ$  for the complex. The latter will be used since it has several advantages, not the least being that it illustrates the large positive entropies which are involved.

As an example, consider the  $\Delta S^\circ$  value reported by M. Calvin<sup>24</sup> for the following:



$$\Delta S = 73 \text{ e.u.}$$

From equation (3) the entropy of  $\text{CH}_3\text{NH}_2, \text{aq.}$  is estimated to be 29 e.u., which is probably accurate to a few entropy units. Using -25 e.u. for

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<sup>23</sup>It seems remarkable, however, with the large number of stability constants known, that only a dozen or so  $\Delta S$  values have been reported for organo-metallic species.

<sup>24</sup>As reported in H. S. Frank and M. W. Evans, J. Chem. Phys. 13, 507 (1945).

$\text{Ni}^{+2}$ , aq.,<sup>25</sup> the entropy of  $\text{Ni}(\text{CH}_3\text{NH}_2)_6^{+2}$  is calculated to be 222 e.u. (compared to  $\text{Ni}(\text{NH}_3)_6^{+2}$ ,  $\bar{S}^0 = 111$  e.u.). The value can easily be in error by 10-15 e.u. due to the entropy of  $\text{CH}_3\text{NH}_2$ , aq., and  $\Delta S$  is probably accurate only to  $\pm 10$  e.u. Thus the entropy of  $\text{Ni}(\text{CH}_3\text{NH}_2)_6^{+2}$  is only accurate to about 20 e.u.;  $222 \pm 20$ . Large errors are, in general, to be expected in these systems, since most entropy values for organic complex ions have been obtained from temperature coefficient data, and previous experience on inorganic species indicates that such calculated values frequently differ from direct calorimetric determinations by sizeable amounts; further, little attempt has been made by investigators in this field to correct their data to zero ionic strength. As Young has recently pointed out,<sup>26</sup> such data not corrected cannot be considered but as an approximation to the correct thermodynamic properties. Nevertheless, the data is semi-quantitatively useful since such large numbers are involved and  $\pm 20$  e.u. in 200 e.u. is only a 10 percent error. The calculated value is obtained from equation (2) with  $N = 13$ , and considering the  $\text{CH}_3 - \text{NH}_2 - \text{Cu}^{+2} - \text{NH}_2 - \text{CH}_3$  to have four branched  $\text{NH}_2 - \text{CH}_3$  groups. To approximate the molar volume, a value can be obtained by assuming the volume of six  $\text{CH}_3\text{NH}_2$  molecules remains unchanged when added to the  $\text{Cu}^{+2}$  ion, but that its added mass changes the density and hence lowers the molar volume. Thus,

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<sup>25</sup> Estimated by the method given in reference 1; (for comparison:  $\text{Cu}^{+2}$ , -23.6 e.u.;  $\text{Mn}^{+2}$ , -20 e.u.;  $\text{Fe}^{+2}$ , -27.1 e.u.).

<sup>26</sup>T. F. Young, "Annual Review of Physical Chemistry," Vol.3, Annual Reviews, Stanford, California, 1952, p. 275.

$$V_m \approx \frac{6(40)}{1.3} \approx 184 \text{ cc.}$$

$\bar{S}^1$  is then calculated to be about 94 e.u., and  $\bar{S}^0 = 94 + 6S^0(\text{H}_2\text{O}) \approx 194$  e.u. Comparison of this value with the one observed above,  $222 \pm 20$ , seems to be satisfactory in view of the fact that the latter was obtained from data not corrected to infinite dilution.

In a similar manner, entropies have been calculated for other species and are given in Table 3. No attempt has been made to include all of the data available, and Table 3 contains only some selected systems to illustrate the principles involved. Since many of the values reported by various observers are frequently in disagreement,<sup>27</sup> it is believed that the average agreement obtained of 10-20 percent is all one can expect. The method proposed here for the calculation of entropy cannot be rigorously tested until the true thermodynamic constants are available, including calorimetric data on complexing.

The determination of the densities of pure complex species or similar species will also be necessary for the close estimation of the molar

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<sup>27</sup> To illustrate this point, M. Calvin and R. Bales (J. Am. Chem. Soc. 68, 953 (1946)) report  $\Delta S = 2$  e.u. for the reaction  $\text{Ni}^{+2} + 3 \text{en} = \text{Ni}(\text{en})_3^{+2}$ , while F. Basolo and R. K. Murmann (J. Am. Chem. Soc. 74, 5243 (1952)) report  $\Delta S = 41$ . Further, Basolo and Murmann obtain 34 e.u. for the reaction  $\text{Ni}^{+2} + 2\text{en} = \text{Ni}(\text{en})_2^{+2}$ , while H. Irving (private communication in previous reference) reports -27 e.u. We find it hard to understand the small or negative entropies of reactions for these systems and have accordingly used Basolo's and Murmann's results in Table 3. The value they report for similar  $\text{Cu}^{+2}$  ion complexing is also in agreement. (See also reference 26.)

volumes, especially for the more complex ions where the term  $0.22 Vm$  becomes important.

Table 3

Comparison of Observed and Calculated Entropies for Metallorganic Ion.							
System	$\Delta S_{obs.}$ (e.u.)	$\bar{S}^0_{ligand}$ (e.u.)	$\bar{S}^0_{complex}$ (e.u.)	$\bar{S}^1_{complex}$ calc. (e.u.)	"n" (number of H <sub>2</sub> O's replaced)	$\bar{S}^0 = \bar{S}^1 +$ $nS^0(H_2O)$ (e.u.)	
6CH <sub>3</sub> NH <sub>2</sub> + Ni <sup>++</sup> (24)	73	29	222	94	6	194	
Triene + Ni <sup>++</sup> (28) Zn <sup>++</sup>	24	85	84	92	2	82	
Mn <sup>++</sup>	43		102				+10
Cd <sup>++</sup>	12		77				
	38		108				
Diene + Ni <sup>++</sup> (28)	10.2	72	57	54	2	98	
Zn <sup>++</sup>	15.9		62				+6
Mn <sup>++</sup>	5.2		55				
Fe <sup>++</sup>	-1.3		44				
3 en + Ni <sup>++</sup> (29)	41	46	154	63	6	163	
3 triene + 2 Mn <sup>++</sup>	0	85	215	209	4	190	
Cd <sup>++</sup>	0		225				+10
(28) Fe <sup>++</sup>	-12		189				-40 <sup>(a)</sup>
Co <sup>++</sup>	2		207				(14 rings) 12
2 diene + Mn <sup>++</sup> (28) Fe <sup>++</sup>	-3.7	72	120	114	4	150	
Co <sup>++</sup>	-7.7		109				+3
Ni <sup>++</sup>	-5.4		114				
	-6.0		113				
3 Dipy(30) + Fe <sup>++</sup>	~0	52	~130	50 <sup>(a)</sup>	6	150	
Dipy(30) + H <sup>+</sup>	13	52	65	38	2	71	

(a) The entropies for these species were estimated from the expression  $\bar{S}^0 = 10 + 3/2 R \ln M + 10.1(n) - 0.1(n)^2 - S^0(s) - 0.22 Vm$  instead of equation (3) which is no longer valid for large "n" values (see text). In the case of Fe(dipy)<sub>3</sub><sup>2+</sup>, the value predicted by equation (3) is approximately 100 e.u. too large.

<sup>28</sup>Jonassen, Hurst, LeBlanc, and Meibohm, J. Phys. Chem. 56, 16  
(1952).

<sup>29</sup>F. Basolo and R. K. Murmann, J. Am. Chem. Soc. 74, 5243  
(1952), see also reference 27.

<sup>30</sup>J. H. Baxendale and P. George, Trans. Faraday Soc. 46, 55  
(1950).

There are a few interesting features to be noted in Table 3. A criteria for internal consistency of a sequence of cations with a given complexing agent can be found in the constancy of the sum of the  $\Delta S$  value and the entropy of the ion being complexed. This results from the fact that the theory does not distinguish between ions forming the same type of complex, except for the small changes in  $V_m$  due to differences in mass. This is borne out by the experimental results in Table 3. Further, the requirement that the structure of the ion need be known in detail is not crucial, especially with chelate compounds. In these latter compounds further coordination is aided by the gain of 2(16.7 e.u.) per two water molecules released, but hindered by the loss of 14 e.u. per chelate ring formed. Also, in some structures, the entry of the metallic ion into further coordination may produce more than one ring with the net result being little change in the total entropy of the compound, as illustrated in Table 3 by the  $M_2\text{trien}_3$  chelates. As one proceeds to smaller and fewer organic ligands, the observed entropies will in general be smaller than the calculated values, due to the fact that our original hypothesis of "burying" the charge of the ion in a hydrocarbon matrix is no longer valid. The data have also been summarized in Figure 1.

#### COMPLICATED SYSTEMS

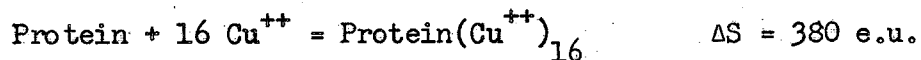
It is of interest to extend the treatment to some very complex species. Klotz and Curme<sup>31</sup> have reported on the successive complexing

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<sup>31</sup>I. M. Klotz and H. G. Curme, J. Am. Chem. Soc. 70, 939 (1948).



of bovine serum albumin by cupric ions, from which we shall choose the reaction:



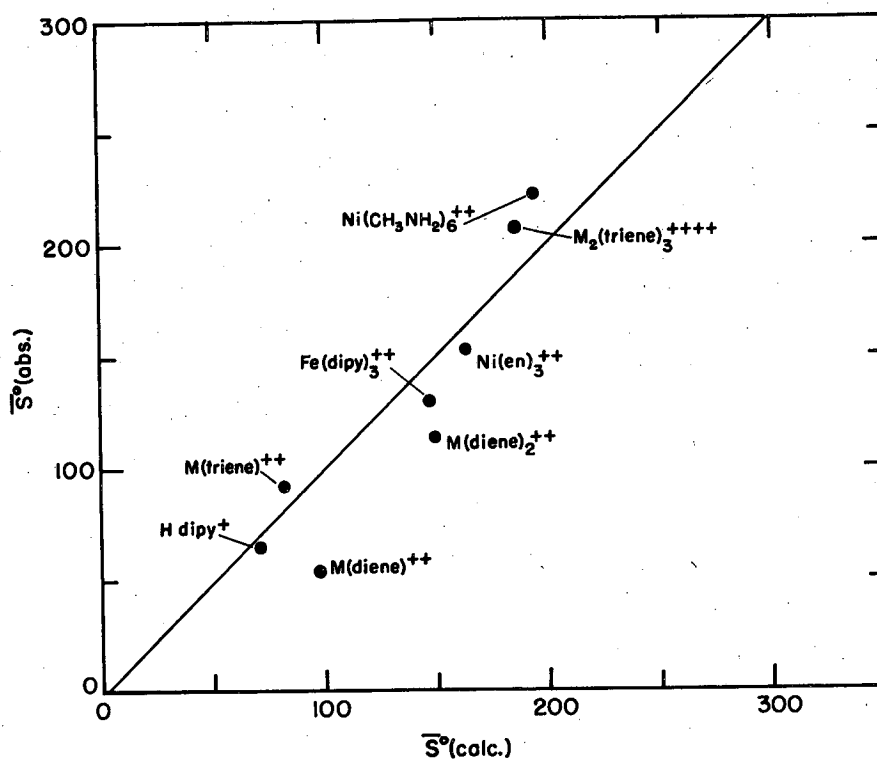
While this value is very large, it represents only a very small change in the total entropy of the protein: ( $\bar{S}_{(\text{est.})}^0 \approx 2 \times 10^4 \text{ e.u.}$ ). Nevertheless, the  $\Delta S$  value can be thought of as involving the creation of a ring with each  $\text{Cu}^{+2}$  ion that goes on the protein molecule with a loss of two water molecules per bound ion. Therefore, the calculated value for  $\Delta S$  above is  $16(9)$ , change in numbers of atoms, minus  $16(14)$ , formation of rings, plus  $32(16.7)$ , loss of water molecules from  $\text{Cu}^{+2}$  ions, giving  $\Delta S = 454 \text{ e.u.}$ , compared to 380 observed. The discrepancy probably lies in our inability to accurately compute the small molar volume change, although even a very small change in this value might affect the entropy markedly for such macro-molecules. Nevertheless, we believe that the average entropy change per cupric ion, 28 e.u. (obs.: 29-18), is in reasonable agreement with the observed values, especially when it is considered that the solutions may be extremely non-ideal. The method should be generally useful in estimating temperature coefficients for systems of biological interest.

#### CONCLUSION

An extension has been developed to the equation of Powell and Latimer for the calculation of the entropy of aqueous solutes from structural considerations. The applicability and accuracy of the proposed method have been demonstrated and some applications have been made to the calculation of the entropies of organo-metallic complex ions and biological systems.

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Figure 1. Comparison of observed and calculated partial molal entropies for organo-metallic complex ions and chelates.