"small amounts of chloride" permanently prevent oscillation are less easy to explain. However, neither of these authors reports how much chloride was added, and in some of his experiments Zhabotinskii[6] employs BrO_3^- concentrations lower than in ours, while the acetyl acetone system[8] exhibits a much more rapid cessation of oscillations, even in the absence of chloride, than the malonic acid system. Thus, in both sets of experiments the threshold value of $[Cl^-]$ for elimination of oscillations noted above may well have been exceeded. It should also be noted that at some Cl^- concentrations, oscillations resume only after an inhibition period of 10-15 h.

Finally, we wish to point out that the mechanism proposed here is by no means the only one which may account for the effects of added chloride in the Belousov reaction. While our experimental results are in good agreement with this mechanism, the number of possible intermediates and steps in such a complex system is truly overwhelming. Current interest in the Belousov reaction and the possible relation between inhibition/modification of this oscillating reaction and of other, biologically important analogues should ensure that the phenomena discussed here will receive the further attention that they deserve.

Experimental Section

Materials. Ceric ammonium nitrate, malonic acid, potassium bromate, sulfuric acid, and potassium chloride were of the highest purity available from commercial sources, as were the salts used in the anion addition experiments discussed in the final section.

Methods. Cerium, malonic acid, and bromate solutions were prepared in sulfuric acid. The reagents were added in the order: cerium, chloride, malonic acid, bromate. The chloride was added from a 50- or 100-μl graduated hypodermic syringe, and mixing time was estimated to be about 1 s. All measurements were carried out at 25 °C.

The [Ce(IV)]/[Ce(III)] ratio was monitored by recording the potential between a platinum electrode and a double junction reference electrode constructed by immersing an Ag|AgCl reference electrode in a reference electrode sleeve (Fisher) filled with a saturated solution of KNO_3, which was in contact with the reaction mixture.

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Structural Entropy Changes in Infinitely Dilute Solutions and Pure Liquids

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Abstract: A molar structural entropy change is defined which measures the change in the structural order of an infinitely dilute solution caused by the introduction of the solute, or the degree of structural order in a pure liquid, based upon the mixing of hard spheres as a reference process. Some values, calculated using scaled-particle theory and experimental entropy data, are reported which demonstrate that nonpolar solute molecules cause large increases in the degree of structural ordering in water compared to nonpolar solvents.

The anomalously large and negative entropy of solution in water which is exhibited by nonpolar liquids and gases, as compared to entropies of solution in other solvents, has generally been interpreted as evidence that the dissolved solute molecules cause an increase in the spatial ordering or structuring of the surrounding water molecules.[1] Kauzmann[2] has pointed out the significance of this solvent structuring to the hydrophobic interaction in proteins (the tendency of nonpolar groups to cluster together in water). While the molecular details of this structuring effect cannot be determined by purely thermodynamic measurements, entropies of solution can provide information about the relative magnitudes of the structuring induced by a solute in different solvents.

This paper defines a new thermodynamic solvation entropy, called the molar structural entropy change, which is characteristic of the change in structural order of an infinitely dilute liquid solution when a solute is introduced from the gas phase. The definition is based upon the mixing of hard spheres, of appropriate size and at the same density as the solution, as a reference process. An analogous treatment of the condensation of a vapor allows one to define a molar structural entropy change which measures the degree of structural order in a pure liquid. The next two sections give physical interpretations of these structural entropies, and derive the equations needed to evaluate them from experimental quantities. The last section applies the equations to several aqueous and nonaqueous solutions and liquids, and discusses the relation of the structural entropies defined here to entropies derived from other treatments of solutions and liquids.

Dilute Solutions

In the Appendix it is shown that $\Delta s_c^0(\mathrm{g} \rightarrow \mathrm{soln})$, the standard molar entropy of transfer of a solute species from an ideal gas phase to an infinitely dilute liquid solution at constant pressure and temperature based on standard states of unit concentration (i.e., unit amount of substance per unit volume) in both phases, is equal to the entropy change in the following hypothetical process. Unit amount (e.g., 1 mol) of solute molecules which are constrained to be nonrotating are transferred from fixed positions in the gas phase to fixed positions in a large amount of the solution phase.[3] During this process, the volume of the gas phase is decreased, and the volume of the solution phase is increased, by the partial molar volumes of the solute species in the respective phases. (These are the volume changes that would occur in the real phases, i.e., ones with freely moving molecules, during the transfer at constant pressure and temperature.) Since the immobile solute molecules have no translational or rotational entropy, the entropy change in this hypothetical process may be considered to be the entropy change of the solvent only.

In order to relate the experimental quantity $\Delta s_c^0(\mathrm{g} \rightarrow \mathrm{soln})$ to a structural entropy, we will consider a sequence of six isothermal steps at thermodynamic temperature T in which one molecule is transferred from gas to solution by the above hypothetical process and the net entropy change ΔS is thus equal to $\Delta s_c^0(\mathrm{g} \rightarrow \mathrm{soln})/N_0$ where N_0 is the Avogadro constant.

Step 1. A large amount of the ideal gas phase at pressure p which includes one solute molecule constrained to a nonrotating, fixed position is decreased in volume by the volume per molecule which is equal to RT/pN_0. R being the gas constant. The entropy change of this compression is $-R/N_0$.

Step 2. The molecules of a large amount of liquid solvent are discharged at constant volume to a fluid of hard spheres having a diameter a which is appropriate to the size of the hard cores of the real molecules. That is, the attractive intermolecular potential of the molecules is removed and the repulsive potential is changed to a hard-sphere potential. Let ΔS_{dis} be the entropy change in this discharge step. The value of ΔS_{dis} should be very small if the solvent molecules are approximately spherical in shape and have no intermolecular forces which could couple their rotations, since in this case the structure of the liquid is determined mainly by the packing of the spherical hard cores and so is almost the same as the structure of the hard-sphere fluid at the same density.[4] The deviation of ΔS_{dis} from zero is a measure of the difference in structure between the packing arrangements in the real liquid and in the hard-sphere fluid at the same density.

Step 3. The volume of the hard-sphere fluid is expanded by an amount v_{B}/N_0, where v_{B} is the partial molar volume of the solute in the real solution at infinite dilution. The entropy change is equal to q_{rev}/T, where q_{rev} is the reversible heat. Since the internal energy of the hard-sphere fluid does not change during an expansion at constant T, the first law of thermodynamics tells us that q_{rev} is equal to the reversible work $w_{\mathrm{rev}} = \int p_{\mathrm{HS}}\, \mathrm{d}V$ where p_{HS} is the pressure of the hard-sphere fluid at the given density and temperature. (As the hard spheres have no attractive forces, p_{HS} is much greater in value than the pressure of the real liquid.) Taking p_{HS} as constant during the expansion, we obtain an expansion entropy equal to $p_{\mathrm{HS}}v_{\mathrm{B}}/N_0T$.

Step 4. A spherical cavity having a diameter b which is appropriate to the size of the hard core of the solute molecule is formed in a fixed position in the hard-sphere fluid at constant volume. The entropy change is equal to $-W/T$ where W is the reversible work of forming the cavity. The value of the cavity entropy is negative because the cavity excludes the hard-sphere particles and decreases their translational freedom. To some extent the effect of forming the cavity is compensated by the increase in translational freedom during the expansion of step 3; nevertheless, the sum of the entropy changes in steps 3 and 4 has a negative value when the cavity is of molecular dimensions.

Step 5. The hard-sphere particles are charged at constant volume to give the real solvent molecules surrounding the cavity. The entropy change, written ΔS_{chr}, is expected to be very small for spherical solvent molecules having no rotational correlations for the same reason that ΔS_{dis} is expected to be small for such molecules.

Step 6. The solute molecule is transferred from its fixed position in the gas phase into a fixed, nonrotating position in the cavity where it can interact with the surrounding solvent molecules. The entropy of this interaction, ΔS_{int}, should be very small if the solute molecule is spherical and has no rotational correlations with the solvent; otherwise, ΔS_{int} is a measure of the changes in spatial arrangements of the solvent molecules as they accommodate themselves to the potential of the immobile solute molecule.

The net entropy change ΔS is the sum of the entropy changes of the six steps:

$$\Delta S = -R/N_0 + \Delta S_{\mathrm{dis}} + p_{\mathrm{HS}}v_{\mathrm{B}}/N_0T - W/T + \Delta S_{\mathrm{chr}} + \Delta S_{\mathrm{int}} \quad (1)$$

If both the solvent and solute molecules are spherical and have no intermolecular orientational forces, the structure of the solvent surrounding the solute molecule is approximately the same as in a hard-sphere mixture and the terms ΔS_{dis}, ΔS_{chr}, and ΔS_{int} are very small. In general, however, when these conditions are not met the sum $\Delta S_{\mathrm{dis}} + \Delta S_{\mathrm{chr}} + \Delta S_{\mathrm{int}}$ is not equal to zero. The value of this sum is a quantitative measure of the structural change in the transfer process, compared to the structural change for mixing hard spheres at the same density. Thus the molar structural entropy change, written Δs_{str}, will be defined by

$$\Delta s_{\mathrm{str}} = N_0(\Delta S_{\mathrm{dis}} + \Delta S_{\mathrm{chr}} + \Delta S_{\mathrm{int}}) \quad (2)$$

The quantity Δs_{str} may contain two different types of contributions. (1) There may be changes induced by a solute molecule in the probabilities of the various spatial arrangements of the surrounding solvent molecules with respect to one another, as compared to the bulk solvent. In a solvent with dipole-dipole or other orientational forces, even a hard-sphere particle can cause this kind of change giving a nonzero value of the sum $\Delta S_{\mathrm{dis}} + \Delta S_{\mathrm{chr}}$. In water, for instance, extensive changes must occur in the intermolecular hydrogen-bonding arrangements of each water molecule in the layers adjacent to a hard sphere because of the anisotropic forces experienced by the molecule there.[5] If there are also orientational forces between the solvent and solute molecules, further changes in solvent structure may occur, contributing to a nonzero ΔS_{int} term. (2) If hydrogen bonds, forces between bond dipoles, or other orienting forces exist between the solute molecule and the surrounding solvent, there is a negative contribution to ΔS_{int} due to the alignment of the solvent molecules with the solute molecule and a consequent decrease in their rotational freedom when the solute molecule is immobile. In a real solution, in which the solute molecules are free to rotate, this effect manifests itself as a correlation between the instantaneous rotational orientations of adjacent solvent and solute molecules. The solvent structure tends to "stick to" the solute molecule.

The first type of contribution to Δs_{str} may be said to measure the change in the solvent structure; the contribution may be positive or negative. The second type of contribution may be said to measure the formation of a structure between the solvent and solute molecules, and should be negative corresponding to an increase in structural order.

From eq 1 and 2, and the fact that $\Delta s_c{}^0(g \rightarrow soln)$ is equal to $N_0\Delta S$, we obtain an expression from which Δs_{str} may be evaluated:

$$\Delta s_{str} = \Delta s_c{}^0(g \rightarrow soln) + R - p_{HS}v_B/T + N_0W/T \quad (3)$$

The pressure of the hard-sphere fluid, p_{HS}, may be obtained from the equation of state found by Carnahan and Starling[6] to give the best agreement with molecular-dynamics data:

$$p_{HS} = (RT/v_A)(1 + y + y^2 - y^3)/(1 - y)^3 \quad (4)$$

where v_A is the molar volume of the hard spheres (equal to the molar volume of the real solvent) and y is the compactness factor[7] given by $y = \pi a^3 N_0/6v_A$. Scaled-particle theory[8] provides a formula for the reversible work, W, of forming a cavity of diameter b in a fluid of hard spheres of diameter a at constant volume and temperature which may be written

$$W = (RT/N_0)[3xy(1 + x)/(1 - y) + (9/2)x^2y^2/(1 - y)^2 - \ln(1 - y)] + \pi b^3 p_{HS}/6 \quad (5)$$

where $x = a/b$. Thus Δs_{str} may be evaluated for any solvent-solute pair from eq 3 with the aid of eq 4 and 5. The quantities for which values are required are the standard molar entropy of solution $\Delta s_c{}^0(g \rightarrow soln)$ (with standard states based on concentration), the molar volume of the solvent, v_A, the partial molar volume of the solute at infinite dilution, v_B, and the effective hard-core diameters a and b for solvent and solute, respectively.

Pure Liquids

We may extend these ideas to the condensation of a vapor, which is a transfer of molecules from the gas phase to the pure liquid. The Appendix shows that the standard molar entropy of this transfer, $\Delta s_c{}^0(g \rightarrow liq)$, using unit concentrations as the standard states, is equal to the entropy of transferring unit amount of nonrotating molecules of the substance from fixed positions in the gas phase to fixed positions in a large amount of the liquid containing freely moving molecules of the same substance.[3] During this process the volume of the gas is decreased, and the volume of the liquid is increased, by the molar volumes of the substance in the respective phases. Since this process is essentially the same as the one involving immobile solute molecules in the case of dilute solutions (except that now the fixed and moving molecules are identical), we may similarly derive a molar structural entropy change given by

$$\Delta s_{str} = \Delta s_c{}^0(g \rightarrow liq) + R - p_{HS}v_A/T + N_0W/T \quad (6)$$

where v_A is the molar volume of the pure liquid. Equation 4 may be used to obtain p_{HS} (with a equal to the effective hard-core diameter of the molecules), and W may be obtained from eq 5 by setting x equal to 1.

It is clear that when a molecule of a substance is introduced into a liquid containing molecules of the same substance, the spatial arrangements of these molecules with respect to one another are the same as in the initial liquid. Thus, in the case of condensation Δs_{str} measures an intrinsic structure of the liquid rather than a change in the structure. It may be readily shown that Δs_{str} is the difference in the entropies of unit amount of the real liquid and unit amount of a hard-sphere fluid at the same density. Furthermore, Δs_{str} consists entirely of the second type of contribution mentioned in the preceding section, caused by orienting forces between adjacent molecules which restrict their rotational freedom. In a liquid of spherical molecules having no rotational correlations, the value of Δs_{str} is expected to be close to zero.

Table I. Experimental Data and Calculated Structural Entropies for Dilute Solutions at 298.15 K

Solute	v_B, cm^3/mol	$\Delta s_c{}^0(g \rightarrow soln)$, J/(K mol)	Δs_{str},[a] J/(K mol)
		Solvent: H_2O	
Ar	31.7 ± 0.4[b]	−68[k]	−55 ± 1
CH_4	37.4 ± 0.4[b]	−72.4[l]	−54 ± 1
C_2H_6	53.3 ± 0.8[b]	−92.2[l]	−76 ± 2
C_6H_6	83.1 ± 0.4[c]	−96.5[l]	−79 ± 1
		Solvent: C_6H_6	
Ar	44.6 ± 0.4[d]	−7.7[m]	4.8 ± 0.5
CH_4	56.1 ± 1.0[e]	−9.0[m]	1 ± 1
C_2H_6	72.0 ± 1.0[e]	−19.2[m]	−6 ± 1
CF_4	82.3 ± 0.8[d]	−7.8[m]	−13 ± 1
SF_6	97.1 ± 1.0[d]	−13.6[m]	−11 ± 1
		Solvent: CCl_4	
Ar	44[f]	−10.4[m]	5
CH_4	51.8[g]	−12.7[m]	6
C_2H_6	66.0[h]	−23.2[m]	0
CF_4	79.7[i]	−8.1[m]	−4
SF_6	104.0 ± 0.8[j]	−19.2[m]	−19 ± 1
		Solvent: c-C_6H_{12}	
Ar	47.6 ± 0.5[d]	−12.2[m]	0.3 ± 0.6
CF_4	87.4 ± 0.9[d]	−10.5[m]	−14 ± 1
SF_6	101.4 ± 1.0[d]	−17.7[m]	−13 ± 1

[a] Values of the solute hard-sphere diameter b were calculated from eq 7 of P. R. Bienkowski and K. C. Chao, *J. Chem. Phys.*, **62**, 615 (1975), a generalized equation based on an analysis of isothermal compressibility data for argon, krypton, and xenon by means of the hard-sphere equation of state of Carnahan and Starling (ref 6). The required values of the critical volume and critical temperature of each solute were taken as the "selected values" given by A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, *Chem. Rev.*, **68**, 659 (1968); and by J. F. Mathews, *ibid.*, **72**, 71 (1972). The resulting calculated values of b (in Å) were: Ar, 3.27; CH_4, 3.62; C_2H_6, 4.18; CF_4, 4.08; C_6H_6, 5.09; SF_6, 4.62. The uncertainties shown in the last column were calculated from the values of the experimental uncertainties of v_B indicated in the second column, and do not include the effect of uncertainties in the hard-sphere diameters. [b] E. W. Tiepel and K. E. Gubbins, *J. Phys. Chem.*, **76**, 3044 (1972). [c] W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954). [d] J. Walkley and W. I. Jenkins, *Trans. Faraday Soc.*, **64**, 19 (1968). [e] W. Y. Ng and J. Walkley, *J. Phys. Chem.*, **73**, 2274 (1969). [f] J. E. Jolley and J. H. Hildebrand, *J. Am. Chem. Soc.*, **80**, 1050 (1958). [g] J. Horiuti, *Z. Elektrochem.*, **39**, 22 (1933). [h] J. Horiuti, *Sci. Pap. Inst. Phys. Chem. Res.* (*Jpn.*), **17**, 125 (1931). [i] R. H. Schumm and O. L. I. Brown, *J. Am. Chem. Soc.*, **75**, 2520 (1953). [j] H. Hiraoka and J. H. Hildebrand, *J. Phys. Chem.*, **67**, 1919 (1963). [k] C. E. Klots and B. B. Benson, *ibid.*, **67**, 933 (1963). [l] A. Ben-Naim, J. Wilf, and M. Yaacobi, *ibid.*, **77**, 95 (1973). [m] E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973).

Calculations and Discussion

Table I lists values of Δs_{str} calculated for dilute solutions of several nonpolar gases in four solvents, using eq 3-5 with parameter values found in Tables I and II. The results demonstrate that nonpolar solutes cause large increases in the structural ordering of water (negative values of Δs_{str}), in accord with previous experience,[1,2] while they cause smaller changes in the structure of nonpolar solvents and in some instances may even decrease the degree of structuring. The results are sensitive to the values chosen for the molecule hard-sphere diameters, as illustrated by Figure 1. Calcula-

Table II. Experimental Data, Hard-Core Diameters, and Calculated Structural Entropies for Pure Liquids at 298.15 K

Compd	v_A, cm³/mol	a, Å	$\Delta s_c^0(g \rightarrow liq)$, J/(K mol)	Δs_{str}, J/(K mol)
H_2O	18.07	2.75[a]	−58.8	−35.8
CH_3OH	40.73	3.69[b]	−60.9[c]	−34.6
C_2H_5OH	58.68	4.34[b]	−72.7[c]	−38.5
$(CH_3)_2SO$	71.37	4.91[b]	−69.9[d]	−16.2
C_6H_6	89.41	5.26[b]	−50.6[c]	0.3
CCl_4	97.09	5.37[b]	−47.8[c]	0.3
c-C_6H_{12}	108.75	5.63[b]	−49.7[c]	1.7

[a] Determined by Pierotti, ref 13, from the solubility of rare gases in water. [b] Determined by Wilhelm and Battino, ref 7, from solubility data. [c] Calculated from v_A and values of the parameters of the Antoine equation taken from T. Boublík, V. Fried, and E. Hála, "The Vapor Pressure of Pure Substances", Elsevier, Amsterdam, 1973. [d] Calculated from v_A and the dependence of vapor pressure on temperature given by T. B. Douglas, *J. Am. Chem. Soc.*, **70**, 2002 (1948).

tions on other solvent–solute pairs are hampered at present by a general lack of reliable values of the solute partial molar volumes v_B.

It is interesting to note that the calculated values of Δs_{str} listed in Table I for CF_4 and SF_6 dissolved in benzene, carbon tetrachloride, or cyclohexane are negative and fairly large (between −4 and −19 J K^{-1} mol^{-1}), whereas these values might have been expected to be close to zero because the molecules are all nonpolar. While it is possible that the discrepancy is partly due to inappropriate values of the hard-core diameters, the negative values calculated for Δs_{str} in these solutions may represent a structuring due to orienting forces which can exist because the solute molecules contain C–F or S–F bond dipoles and the solvent molecules either have an anisotropic polarizability (in the case of benzene and cyclohexane) or contain C–Cl bond dipoles (in the case of carbon tetrachloride).

Table II lists values of Δs_{str} calculated from eq 6 for seven pure polar and nonpolar liquids. The values show as expected that the polar liquids, especially those capable of forming hydrogen bonds, are much more highly structured than the nonpolar ones.

It has been customary to evaluate structuring in an aqueous solution by measuring the entropy of transfer of the solute to the solution from another condensed phase, which may be pure liquid solute or a reference solution employing a nonpolar solvent.[2,9,10] Kauzmann[2] suggested that an appropriate measure of the change in water structure is the standard molar entropy of this transfer with standard states based on mole fractions, a quantity which we will write as $\Delta s_x^0(\alpha \rightarrow \beta)$ (where α and β designate the two condensed phases).

For the transfer between two dilute solutions of arbitrary composition, or between a pure liquid and a dilute solution, the molar entropy change may be written

$$\Delta s(\alpha \rightarrow \beta) = \Delta s_x^0(\alpha \rightarrow \beta) - R \ln (x_\beta/x_\alpha) \qquad (7)$$

where x_α and x_β are the mole fractions of solute in the two phases. Kauzmann[2] calls $\Delta s_x^0(\alpha \rightarrow \beta)$ the unitary part, and $-R \ln (x_\beta/x_\alpha)$ the cratic part, of the entropy. The concept of a unitary entropy was originally introduced by Gurney[11] to designate a contribution which depends only on the particular kinds of chemical species involved and not on the mole fraction composition of the phases. The cratic contribution, on the other hand, depends only on the composition. (It should be pointed out that *any* standard molar entropy change, such as $\Delta s_c^0(\alpha \rightarrow \beta)$, is a unitary entropy within the sense of Gurney's meaning.)

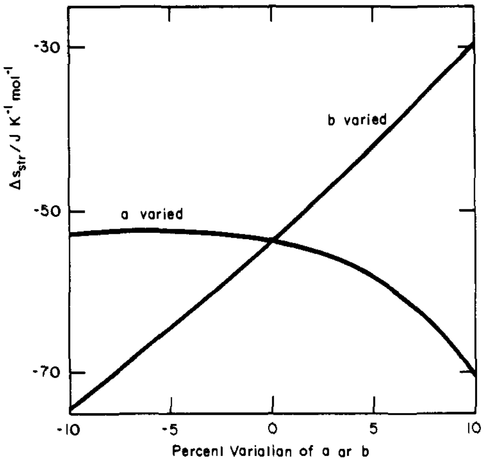

Figure 1. Effect of varying the value of a from 2.75 Å, or the value of b from 3.62 Å, on the calculated value of Δs_{str} for a solution of methane in water at 298.15 K.

The use of the unitary entropy $\Delta s_x^0(\alpha \rightarrow \beta)$ as a structural entropy implies that the transfer process could be viewed as occurring by two particular steps. In the first step, the solute is transferred as if there were no structural changes and the solutions were ideal, giving the cratic entropy $-R \ln (x_\beta/x_\alpha)$. In the second step, the solvent structure in phase β changes with an entropy change equal to the unitary entropy. Thus there is an assumption of ideal mixing in the solutions which may not be justified. It is further assumed that no structural change occurs in the reference phase α as solute molecules are removed, an assumption which is not supported by the results in Tables I and II. These assumptions are absent in the present treatment of structural entropies.

It is not difficult to show that the value of Δs_{str} obtained by the present treatment for the solution in phase β is equal to the unitary entropy $\Delta s_x^0(\alpha \rightarrow \beta)$, provided that the two solvents (or solvent and liquid solute) have equal molecule hard-core diameters and equal molar volumes and the volume change of the transfer is zero. These conditions, if met, ensure that the entropies of liquid expansion and cavity formation during the transfer of the solute from a common gas phase to the two condensed phases are exactly equal, so that they will cancel in the transfer between the two condensed phases. A further condition is that the structural entropy change in phase α must be zero. Since these various conditions do not hold in general, Δs_{str} is in principle a better quantitative guide to changes in structural order than is a unitary entropy.

Two previous applications of scaled-particle theory are related to the present treatment. Pierotti[12] assumed that the free energy of introducing a solute molecule into a solvent at constant pressure and temperature is equal to the reversible work W of forming a cavity of appropriate size in the solvent treated as a fluid of hard cores with an attractive potential (so as to have a pressure of 1 atm); thus the solvent is treated as having the structure of a hard-sphere fluid. The standard molar entropy of solution in Pierotti's method is obtained from $\Delta s_c^0(g \rightarrow soln) = -N_0\, dW/dT$, with W given by scaled-particle theory. The method gives excellent predictions[12] of the entropies of solution of nonpolar gases in nonpolar solvents, which is not surprising; but it also gives good agreement with experimental entropies of solution in water,[13] a result which is quite unexpected[5,14] in view of the known structuring effects in aqueous solutions. Ben-Naim and Friedman[14] have suggested that the difficulty might be resolved by taking into account a temperature dependence of the effective hard-core diameters in evaluating $\mathrm{d}W/\mathrm{d}T$; such a temperature dependence has been found in a number of solvents from gas solubility data.[15] The present treatment is able to avoid the use of temperature derivatives by considering the cavity to be formed in a hard-sphere fluid without attractive forces, so that the molar entropy of cavity formation is $-N_0W/T$.

Yosim and Owens[4] derived an expression for the entropy of vaporization of a liquid which successfully predicts the enthalpies and entropies of vaporization of a variety of nonpolar liquids.[4,16] Their method is closely related to the present treatment of pure liquids; in fact, their expression for the standard molar entropy of vaporization (eq 9 of ref 4) is identical with what one would obtain by solving eq 6 for $-\Delta s_c{}^0(\mathrm{g} \rightarrow \mathrm{liq})$, with W given by eq 5, p_{HS} taken from scaled-particle theory (eq 4 with the term $-y^3$ deleted from the numerator), and Δs_{str} set equal to zero.

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Appendix. Statistical Mechanics of the Transfer Process

The general relation between the entropy S of a closed chemical system of volume V and the partition function Q of the system is

$$S = k\,(\partial[T \ln Q]/\partial T)_V \tag{A-1}$$

where k is the Boltzmann constant and T the thermodynamic temperature. Consider a very dilute liquid solution containing N_{A} molecules of solvent (species A) and N_{B} molecules of solute (species B). Suppose initially that the solvent molecules in this system are free to move, but that the solute molecules are constrained so as to be rigid (no internal motion), nonrotating, and fixed in a stationary position in the system separated from one another by large distances. The partition function Q' of this hypothetical system is obtained from classical statistical mechanics by integrating the appropriate Boltzmann factor over the coordinates and momenta of the solvent molecules, and multiplying by a factor $1/N_{\mathrm{A}}!$ for the indistinguishability of the solvent molecules. Since the solvent molecules feel the potential of the immobile solute molecules, Q' is a function of N_{B} as well as of V, T, and N_{A}. From eq A-1, the entropy S' of the constrained system is given by

$$S' = k\,(\partial[T \ln Q']/\partial T)_{V,N_{\mathrm{A}},N_{\mathrm{B}}}$$

The quantity S' may be regarded as the entropy of N_{A} solvent molecules in the presence of N_{B} immobile solute molecules at the given volume and temperature.

Now consider an unconstrained system containing the real solution (i.e., with freely moving molecules) having the same numbers of molecules and the same volume and temperature as the constrained system. The partition function Q for this system is obtained by integrating Q' over the $3N_{\mathrm{B}}$ translational coordinates, the $3N_{\mathrm{B}}$ Euler rotation angles, the internal coordinates of each solute molecule, and the momenta which are conjugate to all of these coordinates; and by multiplying by the factor $1/N_{\mathrm{B}}!$:

$$Q = (1/N_{\mathrm{B}}!)q_{\mathrm{B}}{}^{N_{\mathrm{B}}}V^{N_{\mathrm{B}}}Q' \tag{A-2}$$

Here, q_{B} is a function only of temperature and is given by

$$q_{\mathrm{B}} = (2\pi mkT/h^2)^{3/2}q_{\mathrm{rot}}q_{\mathrm{int}}$$

where m is the solute molecule mass and q_{rot} and q_{int} are partition functions for the rotational and internal degrees of freedom of a solute molecule. To obtain eq A-2, it was assumed that the solute molecules in the unconstrained system are so far apart on the average that Q' is independent of the translational and rotational coordinates of these molecules. The entropy S of the unconstrained system is obtained from eq A-1 and A-2 with the aid of Sterling's approximation $\ln N_{\mathrm{B}}! = N_{\mathrm{B}} \ln N_{\mathrm{B}} - N_{\mathrm{B}}$, giving

$$S = kN_{\mathrm{B}}[1 - \ln (N_{\mathrm{B}}/V) + \mathrm{d}(T \ln q_{\mathrm{B}})/\mathrm{d}T] + S' \tag{A-3}$$

The partial molar entropy s_{B} of the solute molecules in the unconstrained system may be obtained from the mathematical relation

$$\begin{aligned} s_{\mathrm{B}} &= N_0(\partial S/\partial N_{\mathrm{B}})_{p,T} \\ &= N_0[(\partial S/\partial N_{\mathrm{B}})_{V,T} + (\partial S/\partial V)_{T,N_{\mathrm{B}}}(\partial V/\partial N_{\mathrm{B}})_{p,T}] \end{aligned}$$

where p denotes pressure and N_0 is the Avogadro constant. We set the partial derivative $(\partial V/\partial N_{\mathrm{B}})_{p,T}$ equal to v_{B}/N_0, where v_{B} is the partial molar volume of the solute in the dilute solution. The other two partial derivatives appearing in the right-hand member of the equation are obtained by differentiating eq A-3. The result is the relation

$$s_{\mathrm{B}} = -R \ln (N_0c_{\mathrm{B}}) + R\,\mathrm{d}(T \ln q_{\mathrm{B}})/\mathrm{d}T + s_{\mathrm{B}}' \tag{A-4}$$

where $c_{\mathrm{B}} = N_{\mathrm{B}}/N_0V$ is the solute concentration and the quantity s_{B}' is given by

$$s_{\mathrm{B}}' = N_0(\partial S'/\partial N_{\mathrm{B}})_{V,T} + (\partial S'/\partial V)_{T,N_{\mathrm{B}}}v_{\mathrm{B}}$$

The preceding equation shows that s_{B}' should be interpreted as the change in the entropy of a large amount of the solvent when a unit amount (e.g., 1 mol) of immobile solute molecules is introduced and the volume is increased by an amount v_{B}; i.e., the volume is increased by the amount which keeps the pressure of the real solution constant as the solute is added. (A term $Rc_{\mathrm{B}}v_{\mathrm{B}}$ has been omitted from the right-hand member of eq A-4 because it is vanishingly small in a very dilute solution.)

A pure substance in the liquid or gas phase may be treated in an analogous fashion by letting Q' denote the partition function of a constrained system in which a very small fraction of the molecules are treated as immobile B-type molecules while the remaining A-type molecules are free to move. The partition function of the unconstrained system is then $Q = (N_{\mathrm{A}}!/N!)q_{\mathrm{B}}{}^{N_{\mathrm{B}}}V^{N_{\mathrm{B}}}Q'$ where N is the total number of molecules. (The factor $N_{\mathrm{A}}!/N!$ is needed because in the constrained system there are N_{A} indistinguishable molecules whereas in the unconstrained system there are N indistinguishable molecules.) By the same series of steps as used to obtain eq A-4, we obtain a similar equation for the molar entropy s of the pure substance:

$$s = -R \ln (N_0c) + R\,\mathrm{d}(T \ln q_{\mathrm{B}})/\mathrm{d}T + s' \tag{A-5}$$

Here c is the concentration of the substance and s' is the entropy change in introducing a unit amount of immobile molecules into a large amount of the substance and increasing the volume by the molar volume.

The molar entropy of transferring a species from one phase to another at constant pressure and temperature is equal to the difference of the molar entropy or partial molar entropy in the two phases. For the transfer from phase α to phase β, where each phase is a dilute solution or a pure gas or liquid, we find using eq A-4 and A-5 that in general the molar entropy change is given by

$$\Delta s(\alpha \rightarrow \beta) = -R \ln (c_\beta/c_\alpha) + \Delta s'$$

where c_α and c_β are the concentrations of the species in the two phases. The quantity $\Delta s'$ is the entropy change in isothermally transferring unit amount of nonrotating molecules of the species from fixed positions in phase α to fixed positions in phase β, while decreasing the volume of phase α and increasing the volume of phase β by the partial molar volumes of the species in these phases. In obtaining this expression, we have assumed that the partition functions for the rotational and internal degrees of freedom of the species are the same in both phases so that the term $R\ d(T \ln q_B)/dT$ cancels when taking the difference.

Under hypothetical standard state conditions of unit concentrations in both phases, $\Delta s(\alpha \rightarrow \beta)$ becomes the standard molar entropy of transfer $\Delta s_c{}^0(\alpha \rightarrow \beta)$ (the subscript c denotes standard states based on concentration) and the term $-R \ln (c_\beta/c_\alpha)$ equals zero. Thus $\Delta s_c{}^0(\alpha \rightarrow \beta)$ and $\Delta s'$ are identical.

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Structure and Chemistry of Bis(cyclopentadienyl)-ML$_n$ Complexes

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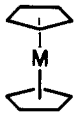
Abstract: A construction of the molecular orbitals of a bent bis(η^5-cyclopentadienyl)M fragment, Cp_2M, M = a transition metal, serves as a starting point for a general account of the electronic structure of Cp_2ML_n molecules, n = 1-3. The following problems are analyzed: the geometry of Cp_2ML_n as a function of the d electron configuration; bonding with π acceptor and donor ligands, emphasizing orbital interactions with conformational consequences such as olefin and carbene orientation and dithiolene bending; distortions of the Cp_2M moiety; insertion reactions of coordinated olefins; carbonyl insertion reactions; oxidative coupling; allyl and tetrahydroborate complexes; triscyclopentadienyl complexes.

The remarkably rich chemistry of bent bis(π-cyclopentadienyl) transition metal complexes[1] is the focus of this study. We proceed to formulate a model for the electronic structure of such molecules, and relate that model to the various known complex types, and the known structures. The eventual goal is an understanding of the chemistry of these molecules.

We begin by considering the valence orbitals of a bent bis(cyclopentadienyl) transition metal fragment. This is followed by a consideration of the interactions of such a fragment with additional ligands with various bonding capabilities.

The Bis(π-cyclopentadienyl) Metal, Cp_2M, Fragment

Normal bis(π-cyclopentadienyl) [bis(η^5-cyclopentadienyl), to be abbreviated throughout this paper as Cp_2] transition metal complexes such as ferrocene are highly symmetric molecules with parallel cyclopentadiene rings (**1**).



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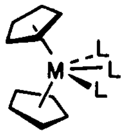

2

Their symmetry is D_{5h} if the two rings are eclipsed, or D_{5d} if the rings are staggered. In bent bis(π-cyclopentadienyl) transition metal complexes the rings are not parallel, that is the angle between the normals to the planes of the cyclopentadienyl ligands is less than 180°, and there are from one to three additional ligands bound to the metal. **2** shows a schematic Cp_2ML_3 structure, for which Cp_2NbH_3 is a real example. A bent Cp_2M fragment has C_{2v} symmetry if the Cp ligands have an eclipsed geometry, and only C_s symmetry if the rings are staggered.

The bonding in the normal metallocenes has been the subject of numerous theoretical and experimental papers[2] and will be discussed here only briefly. In a D_{5d} geometry the π orbitals of two parallel $C_5H_5^-$ ligands yield three sets of approximately degenerate orbitals: a low-lying filled pair of a_{1g} and a_{2u} symmetry, a set of filled orbitals, e_{1g} and e_{1u}, and a high-lying empty set of antibonding orbitals of symmetry e_{2g} and e_{2u}. These interact with the orbitals of the metal as shown in Figure 1, which is a schematic interaction diagram of a normal Cp_2M complex. There is a strong interaction with the metal s and p orbitals and also a strong bonding interaction with the $e_{1g}(d_{xz}, d_{yz})$ set. The remaining three d orbitals of the metal, the $a_{1g}(d_{z^2})$ and the $e_{2g}(d_{x^2-y^2}, d_{xy})$ set, remain essentially nonbonding. Thus the d-level splitting is $e_{2g} \lesssim a_{1g} < e_{1g}{}^*$ or $(d_{x^2-y^2}, d_{xy}) \lesssim (d_{z^2}) < (d_{xz}, d_{yz})$.

Ferrocene is by far the most stable of the metallocenes, which is not surprising, because it has the ideal number of electrons for Cp_2M complexes. Considering each $C_5H_5^-$ ligand as a six-electron donor, together with the six d electrons of Fe(II), one achieves an 18-electron configuration by filling precisely the nonbonding e_{2g} and a_{1g} levels. Cobaltocene, a d^7 — 19 electron complex, and nickelocene, a d^8 — 20 electron complex, each has an excess number of elec-