

solute-solvent interactions

edited by

J.F. Coetzee and Calvin D. Ritchie

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Preface

The majority of reactions that are of chemical or biological interest occur in solution. Until some 50 years ago, it was widely assumed, either explicitly or more often implicitly, that the solvent merely provides an inert medium for chemical reactions. Nevertheless, as long ago as 1883 Arrhenius invoked a specific ionizing interaction of water with electrolytic solutes, a view that subsequently had to be abandoned for the class of ionophoric solutes. Perhaps the first general realization of the significance of solute-solvent interactions came with the development 40 years later of the Franklin-Germann solvent system and the Brønsted-Lowry proton theories of acid-base reactions, both of which evolved mainly as a result of studies carried out in nonaqueous solvents. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become increasingly clear during the past 2 or 3 decades that the properties of the majority of solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, such as water, is substantially modified by the presence of certain solutes. Not only is the study of such interactions of considerable interest *per se*, but it is essential if the intrinsic properties of solutes are to be understood better, unless the reactions can be carried out in the gas phase.

For a variety of well-known reasons, water is of unique importance among solvents. Nevertheless, there can be little doubt that until comparatively recently fundamental studies of nonaqueous solutions had been neglected, with few notable exceptions, such as the pioneering investigations of Walden, Franklin and Kraus. However, during the past decade in particular, a rapidly increasing reservoir of fundamental information on nonaqueous solutions has accumulated, which has broadened perspective and deepened understanding of the spectrum of interactions that can occur in solution. It also has provided new perspectives on the classical and complex problem of aqueous solutions. These rapid developments have provided the main incentive for publishing this treatise.

Solute-solvent interactions are of current interest in all branches of chemistry and in other disciplines as well. Physical chemists and investigators from the other traditional classifications of chemistry are involved in

fundamental studies of these interactions. A considerable part of inorganic chemistry is properly treated as the chemistry of aquo complexes. Organic and inorganic chemists have made extensive use of changes in medium for synthetic purposes. Analytical chemists use similar changes in medium to adjust the driving force of reactions. For these and other reasons, both fundamental and empirical information on solute-solvent interactions can be found in a vast array of journals. The task of collecting, assimilating, and presenting information from such a variety of primary sources has become much too formidable to be handled by a single author. It therefore has been our objective to concentrate on topics that should be of wide interest, and to have these presented by specialists in each area.

Any single volume of reasonable length dealing with the broad topic of solute-solvent interactions must be highly selective. The actual selection of topics necessarily reflects the personal judgment and bias of the editors. We anticipate that the topics that we have omitted may be more open to criticism than those included. We have avoided extensive discussion of subjects that had recently been presented in depth elsewhere. One example is the interaction between solutes and the structure of water. After careful consideration we also have excluded from this volume a detailed discussion of attempts to evaluate free energies of solvation of single ions and of single electrode potentials in different solvents. Although the theoretical significance of these quantities is not quite clear, they are of great operational value. However, the current literature reveals such disagreement on virtually every essential point involved that even the *sign* of the free energy of transfer of many ions from water to many other solvents cannot be given unambiguously. The problem essentially reduces to the fact that we are concerned here with the relatively small difference between two large, inexact free energy values. Fortunately, there are promising signs that the uncertainties now existing in this field may be minimized in the near future by progress in two areas: improved techniques to stabilize and evaluate surface potentials and thereby permit measurement of Galvani potentials, and detailed statistical mechanical calculations of single ion enthalpies. From this optimistic point of view we feel that it would be premature to present a detailed discussion of this important topic at present. Nevertheless, for a limited number of solvents and solvent mixtures certain useful conclusions can be drawn, and certain of these cases are presented in Chapter 2 in the context of the establishment of acidity scales.

The topics included have been selected to acquaint the reader with the general advances that have been made in understanding solvent effects in several representative areas. The first chapter, "Heats and Entropies of

Ionization," contains a critical compilation and discussion of data on the ionization of Brønsted acids in aqueous solution. This chapter is followed by "Medium Effects and pH in Nonaqueous Solvents" in which the basic concepts and techniques for the study of nonaqueous systems are presented. These two chapters serve as an introduction to the remaining ones which treat both aqueous and nonaqueous media, as well as mixed solvents.

We trust that this treatise will stimulate further interest in the study of solute-solvent interactions.

March, 1969

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Contents

PREFACE	v
CONTRIBUTORS	ix

1. Heats and Entropies of Ionization

John W. Larson and Loren G. Hepler

I. Introduction	1
II. General Methods and Thermodynamic Relations	2
III. Ionization of Water	5
IV. Thermodynamic Data for Ionization of Aqueous Acids	7
V. Theoretical Interpretation Involving ΔH and ΔS	22
VI. Additional Data and Comments	37
References	38

2. Medium Effects and pH in Nonaqueous Solvents

Roger G. Bates

I. Introduction	46
II. Nature of the Operational pH Scale	46
III. Effect of Solvent Character	49
IV. Acids and Bases in Amphiprotic Media.	53
V. Hydrogen-Ion Activity	55
VI. Standard Reference States.	56
VII. Estimation of the Transfer Free Energy of Single Ionic Species	58
VIII. Absolute Hydrogen-Electrode Potentials	67
IX. Nature of the Medium Effect	71
X. Choice of a Practical pH Unit	79

XI. Acidity Scale for Deuterium Oxide	85
XII. Acidic and Basic Solvents.	87
XIII. Aprotic Solvents	89
References	93

3. Acidity Functions

Richard H. Boyd

I. Introduction	98
II. Definition of the Acidity Function	100
III. Acidity Functions for Aqueous Acid Solutions.	105
IV. Interpretation of Acidity Function Behavior in Aqueous Acids	128
V. Acidic Nonaqueous or Mixed Solvent Systems.	158
VI. Acidity Functions in Strongly Basic Solutions	167
VII. Application of Acidity Functions to Kinetics	168
VIII. Experimental Methods	172
Appendixes	178
References	213

4. Interactions in Dipolar Aprotic Solvents

Calvin D. Ritchie

I. Introduction	219
II. Acidities in Dipolar Aprotic Solvents	221
III. Rates of Proton-Transfer Reactions.	246
IV. Solvent Effects on the S_N1 Reaction.	272
V. Solvent Effects on S_N2 Reactions	284
VI. Dipolar and Multipolar Complexes	290
References	294

5. The Selective Solvation of Ions in Mixed Solvents

H. Schneider

I. Introduction	301
II. The Free Energy of Solvation	303

III. Determination of Selective Solvation	305
IV. Salting-Out and Salting-In	329
References	338

6. Solvent Isotope Effect on Thermodynamics of Nonreacting Solutes

Edward M. Arnett and Donald R. McKelvey

I. Introduction	344
II. The "Water Problem" and Solvent Isotope Effects	347
III. Thermodynamic Properties of Transfer from H ₂ O to D ₂ O	355
IV. Summary and Conclusions	390
Appendix	392
List of Symbols.	394
References	395

7. Solvent Isotope Effects for Equilibria and Reactions

P. M. Laughton and R. E. Robertson

I. Introduction	400
II. Water Characteristics and SIE's in Equilibria and Kinetics	401
III. Ionization of Acids	403
IV. Nucleophilic Substitution and SIE's	424
V. KSIE's and Acid Catalysis	433
VI. KSIE and Base Catalysis	473
VII. Miscellaneous Organic Reactions	499
VIII. Oxidation-Reduction	503
IX. Inorganic Reactions	508
X. Reactions Promoted by Radiation	516
XI. Non-aqueous Solvents	522
XII. Conclusion	522
References	525

8. Organoalkali Compounds in Ethers

John F. Garst

I. Introduction	539
II. General Considerations	543

III. Some More Detailed Aspects and Miscellaneous Topics . .	576
IV. Summary	599
Abbreviations Used for Solvents	599
List of Symbols.	600
References	601
 Appendix: Recommended Purification Methods for Selected Solvents . .	607
 J. F. Coetzee and Calvin D. Ritchie	
 AUTHOR INDEX	609
 SUBJECT INDEX	639

1

Heats and Entropies of Ionization

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I. Introduction	1
II. General Methods and Thermodynamic Relations	2
III. Ionization of Water	5
IV. Thermodynamic Data for Ionization of Aqueous Acids	7
V. Theoretical Interpretation Involving ΔH and ΔS	22
VI. Additional Data and Comments	37
References	38

I. Introduction

This chapter is primarily concerned with the thermodynamics of ionization of aqueous acids, a subject which is of both practical and theoretical importance. We shall begin by considering the general methods that have been applied and can be applied to determination of such data, and then tabulate data for self-ionization of water and for ionization of a large number of aqueous acids. Although most recent work has focused on ΔH^0 and ΔS^0 values and much of our attention is similarly focused,

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we also tabulate other data (ΔG° and ΔC_p°) and call attention to investigations in which these thermodynamic variables have been of special interest.

The utility of the data we consider here for classical thermodynamic calculations has been widely known for many years and need not receive special attention from us. Rather, we are especially concerned with the relevance of these thermodynamic data to a variety of other problems. For example, considerations of thermodynamic data for aqueous species and reactions in aqueous solutions have contributed importantly to our growing understanding of solute-solvent interactions, microscopic structures of solutions, and linear free-energy relations.

II. General Methods and Thermodynamic Relations

The general principles of thermodynamics that are applicable to solutions and processes in solution have been developed in a variety of excellent texts (1), so we merely summarize the results in the form of useful thermodynamic equations.

The Gibbs free energy (relevant to systems maintained at constant pressure) is related to the enthalpy (heat) and entropy by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1-1)$$

Here and elsewhere we have used the superscript zero to indicate that the thermodynamic function applies to species in some appropriate standard state. The standard free energy change associated with a reaction is related to the equilibrium constant for the reaction by

$$\Delta G^\circ = -RT \ln K \quad (1-2)$$

Numerical values of both ΔG° and K depend on the choice of standard states and the associated choice of how concentrations are to be expressed—a problem that becomes important in comparisons involving different solvents.

The variation of the equilibrium constant K with absolute temperature T is given by the van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (1-3)$$

The variation of the enthalpy or heat of reaction is given by the Kirchhoff equation:

$$\frac{d\Delta H^\circ}{dT} = \Delta C_p^\circ \quad (1-4)$$

Thus if one has values for the equilibrium constant at a series of temperatures, successive differentiations can yield values for both ΔH° and ΔC_p° . Then further use of Eqs. (1-1) and (1-2) permits evaluation of both ΔG° and ΔS° . Conversely, if one has numerical values for K and ΔH° at one temperature and for ΔC_p° over the temperature range of interest, it is possible to calculate values of K , ΔG° , ΔH° , and ΔS° over this same temperature range.

A simple and common use of Eq. (1-3) involves integration for the special case where ΔH° is independent of temperature, leading to

$$\ln K = -\frac{\Delta H^\circ}{RT} + \text{constant} \quad (1-5)$$

For most reactions of present interest, $\Delta C_p^\circ \neq 0$ and ΔH° consequently depends on the temperature. Thus Eq. (1-5) is an approximation that often yields ΔH° and ΔS° values of unsatisfactory accuracy.

The usual means of allowing for the temperature dependence of ΔH° has been to express ΔC_p° as some function of temperature so that Eq. (1-4) can be integrated to yield an expression for ΔH° as a related function of temperature. Then this expression permits integration of the van't Hoff equation (1-3) to obtain the desired equation for $\ln K$ as a function of temperature. It is possible to use experimental K values at several temperatures with this final equation to fix the values of the parameters in the original expression of ΔC_p° as a function of temperature. These values then permit calculation of the desired ΔH° , ΔS° , and ΔC_p° over the range of temperature covered by the K values. In making some of these calculations it may be convenient to use the equation for the temperature dependence of the entropy change, which is

$$\frac{d\Delta S^\circ}{dT} = \frac{\Delta C_p^\circ}{T} \quad (1-6)$$

The difficulties and uncertainties associated with these calculations are partly derived from the inevitable experimental errors in the K values and partly from the calculator's choice of the function that represents the dependence of ΔC_p° on temperature. These questions have been considered in detail recently by King (2) and Ives and Marsden (3). Some results of King's statistical analysis of such calculations are summarized in Table 1-1.

Clarke and Glew (4) have recently developed another method for evaluation of thermodynamic functions from equilibrium constants.

Their method, which involves expression of ΔC_p° as a Taylor's series expansion, is worthy of further attention and comparison with the calculations of Ives and Marsden (3).

TABLE 1-1
Propagation of Errors in pK to Errors in ΔH° , ΔS° , and ΔC_p° at 25° (2)

	Temp. $^\circ\text{C}$					
	20, 22, 24, 26, 28, 30		0, 10, 20, 30, 40, 50		5, 10, 15, 20, 25, 30, 35, 40, 45, 50	
SD in pK^a	0.02	0.001	0.02	0.001	0.02	0.001
SD in ΔH° , cal/mole	970	50	200	10	190	10
SD in ΔS° , cal/deg/mole	3.3	0.16	0.65	0.033	0.32	0.016
SD in ΔC_p° , cal/deg/mole	666	33	27	1.3	28	1.4

^a SD indicates standard deviation.

It is possible to determine equilibrium constants and hence free energies from calorimetric measurements that also yield the enthalpy of reaction. Although this method is subject to important limitations with respect to both accuracy and systems to which it is applicable, it has been applied to investigation of the ionization of acids in aqueous solution. Possibly the most recent investigation of this sort is that of Christensen et al. (5). We later cite data for several acids that have been determined by this or related calorimetric methods.

Calorimetry has also been applied extensively to determination of ΔH values for reactions that are practically complete under the conditions of the measurements. Combination of these ΔH values with appropriate heats of dilution then yields desired ΔH° values. Use of a ΔH° value in Eqs. (1-1) and (1-2) with a value of K at the same temperature leads to ΔS° . We later cite data that have been obtained in this way for a number of acids.

Although calorimetric determination of ΔH° and calculation of ΔH° from the van't Hoff equation are equally sound in principle, actual results obtained in these two ways sometimes differ considerably. The existence of these discrepancies is of particular interest to us for several reasons. First, the ΔH° and ΔS° values for self-ionization of water as

determined from calorimetric data and the van't Hoff equation are not in agreement. This modest disagreement is of special interest because of the importance we attach to water. Second, ΔH° and especially ΔS° values have proved useful in yielding structural information about solute species and solute-solvent interactions. Third, various empirical or theoretical correlations of interest involve ΔH° or ΔS° values.

III. Ionization of Water

Possibly the most quoted thermodynamic data for the ionization of water are those derived from the extensive cell measurements of Harned and several co-workers (6). These values are $\Delta G^\circ = 19.095$ kcal/mole, $\Delta H^\circ = 13.53$ kcal/mole, $\Delta S^\circ = -18.68$ cal/deg/mole, and $\Delta C_p^\circ = -46.6$ cal/deg/mole. Their values for the ionization constant have not been seriously questioned, but there has been some reason to suspect that their ΔH° , ΔS° , and ΔC_p° values based on temperature derivatives may be subject to error or large uncertainties. Some of these doubts appeared to be removed on publication of calorimetric determination of $\Delta H^\circ = 13.50$ kcal/mole by Papee et al. (7).

In spite of the impressive agreement between the two ΔH° values cited above, several recent calorimetric investigations have provided convincing support for earlier calorimetric results that pointed to a ΔH° of ionization less than the apparently established $\Delta H^\circ = 13.50$ or 13.53 kcal/mole.

Since some of the calorimetric measurements have been made at temperatures other than 25°C , it is necessary to consider ΔC_p° for the ionization reaction. The second derivative of $\ln K$ with respect to temperature leads (6) to $\Delta C_p^\circ = -47$ cal/deg/mole. Apparent molal heat capacity data that Parker (8) has tabulated and extrapolated to infinite dilution lead to $\Delta C_p^\circ = -53.5$ cal/deg/mole at 25°C and also to $d(\Delta C_p^\circ)/dT = 0.9$ cal/deg/mole near 25°C . The latter values appear to be most reliable.

Two early calorimetric determinations by Richards et al. (9) of heats of neutralization at temperatures below 25°C now lead to $\Delta H^\circ = 13.35$ kcal/mole for the heat of ionization of water at 25°C . Similar measurements by Gillespie et al. (10) at temperatures both above and below 25°C lead to $\Delta H^\circ = 13.36$ kcal/mole at 25°C . Pitzer's (11) heats of neutralization at 25°C also lead to $\Delta H^\circ = 13.36$ kcal/mole for the ionization of water. Use of what appear to be the best heat of dilution data with the heats of neutralization of Bender and Biermann (12) leads to $\Delta H^\circ = 13.32$

kcal/mole. Similar measurements by Bidinosti and Biermann (13) are not entirely self-consistent but definitely indicate $\Delta H^\circ < 13.5$ kcal/mole. Some of these data lead to $\Delta H^\circ = 13.33$ kcal/mole for ionization of water at 25°C. Other calorimetric investigations by Davies et al. (14) lead to $\Delta H^\circ = 13.36$ kcal/mole, while Sacconi et al. (15) report $\Delta H^\circ = 13.34$ kcal/mole.

Recent and thorough calorimetric investigations by Hale et al. (16) and Vanderzee and Swanson (17) both lead to $\Delta H^\circ = 13.34$ kcal/mole. On the basis of all these results, we adopt $\Delta H^\circ = 13.34$ kcal/mole for ionization of water at 25°C.

Combination of $\Delta H^\circ = 13.34$ kcal/mole with $\Delta G^\circ = 19.095$ kcal/mole from the ionization constant (6) leads to $\Delta S^\circ = -19.30$ cal/deg/mole for ionization of water at 25°C. Since we have $\Delta C_p^\circ = -53.5$ cal/deg/mole at 25°C and $d(\Delta C_p^\circ)/dT = 0.9$ cal/deg²/mole from Parker (8),

$$\Delta C_p^\circ = -321.8 + 0.9T \quad (1-7)$$

Combination of Eqs. (1-4) and (1-7) with ΔH° at 298°K leads to

$$\Delta H^\circ = 69,280 - 321.8T + 0.45T^2 \quad (1-8)$$

Similar combination of Eqs. (1-6) and (1-7) with ΔS° at 298°K leads to

$$\Delta S^\circ = 1545 - 321.8 \ln T + 0.9T \quad (1-9)$$

Insertion of these general equations (all energy units are calories) for ΔH° and ΔS° in Eq. (1-1) gives

$$\Delta G^\circ = 69,280 - 1867.65T + 321.8T \ln T - 0.45T^2 \quad (1-10)$$

Further combination with Eq. (1-2) gives

$$\ln K = -\frac{34,867}{T} + 939.35 - 161.95 \ln T + 0.226T \quad (1-11)$$

These equations, which represent the best available data for ionization of water, are valid in the temperature range near 25°C where $d(\Delta C_p^\circ)/dT = 0.9$ cal/deg²/mole.

Although we are primarily concerned with enthalpy-entropy effects related to temperature dependence of the ionization constant, it is also of value to consider volume effects related to the pressure dependence of the ionization constant. Hamann (18) has determined the ionization constant of water at 25°C at pressures up to 2000 atm. His results lead to $\Delta \bar{V}^\circ = -20.4$ cm³/mole at 1.0 atm for ionization of water. It appears that a more accurate value can be derived from partial molal volume data. From such data we (19) have $\Delta \bar{V}^\circ = -22.11$ cm³/mole.

Several investigations cited later indicate the importance of isotope effects on thermodynamics of solution processes. Possibly the most important reference data in this connection are those for ionization of heavy water, D_2O . Recent emf measurements on a cell without liquid junction have been made by Covington et al. (20) and lead to $\Delta H^\circ = 14.31$ kcal/mole and $\Delta C_p^\circ = -54.8$ cal/deg/mole for the ionization of D_2O at $298^\circ K$.

The question of standard states, which is especially relevant to certain comparisons involving ΔG° and ΔS° , is taken up later in some detail.

IV. Thermodynamic Data for Ionization of Aqueous Acids

Before tabulating thermodynamic data for ionization of aqueous acids, it is well to consider the reliability of the various data. We do this by way of comparison of data (mostly ΔH° and ΔS°) obtained by different investigators using different methods.

Our first example is benzoic acid, which has been investigated many times by several different methods. Calorimetric measurements (21) at 10, 20, and $30^\circ C$ have yielded ΔH° of ionization values at these temperatures and an interpolated $\Delta H^\circ = 110$ cal/mole at $25^\circ C$. Later calorimetric measurements (22) have yielded $\Delta H^\circ = 105$ cal/mole at 25° along with ΔH° values at 15 and $40^\circ C$. All these data are consistent with $\Delta C_p^\circ = -38$ cal/deg/mole. Jones and Parton (23) have calculated $\Delta H^\circ = 104$ cal/mole (at 25°) from their K values at several temperatures. Since uncertainties are about ± 50 cal/mole in the calorimetric values and ± 150 cal/mole in the latter value, we see that the results cited above are in excellent agreement. It should also be noted that Everett and Wynne-Jones (24) have calculated $\Delta H^\circ = 40$ cal/mole from the old (1898) equilibrium data of Schaller.

Calorimetric measurements by Canady et al. (25) led these workers to report $\Delta H^\circ = 90$ cal/mole for ionization of benzoic acid. This value, unlike those cited above, is dependent on the ΔH° for ionization of water. Their reported ΔH° for benzoic acid is based on $\Delta H^\circ = 13.50$ kcal/mole for ionization of water, rather than the almost certainly better value of 13.34 kcal/mole. Using this latter value, we calculate $\Delta H^\circ = -70$ cal/mole for the ionization of benzoic acid from the results of Canady et al.—a value that is not in good agreement with those cited above. The equilibrium data of Briegleb and Bieber (26) lead to $\Delta H^\circ = -420$ cal/mole for ionization of aqueous benzoic acid. The discrepancies between these last two ΔH° values and the “best” values cited in the paragraph above may