SESSION II

I. THEORY AND INTERPRETATION OF ISOTOPE EFFECTS

(B) Isotope effects in H_2O–D_2O mixtures

The Solvent Isotope Effect in H_2O–D_2O Mixtures—A. J. KRESGE, *Illinois Institute of Technology, U.S.A.*

Comment: With regard to the first part of Dr Kresge's paper, dealing with equilibrium constants in mixed H_2O/D_2O media, I agree with the conclusions he reached within his terms of reference, and, in particular, that the Gross–Butler phenomenon would seem to have little value as a mechanistic tool. I cannot, however, accept his claim that the treatment is general. The equations for the Gross–Butler case have been derived several times in the past. In a paper by Long, Paul and myself (cited in Dr Kresge's paper as Reference 7), we outlined a general formulation from which the expression for any degree of polymerization of water and hydration of the proton could be obtained by simple application of the "rule of the geometric mean", *i.e.* statistical distribution of protons and deuterons within each species.

The problem of real significance is whether such a statistical approach, neglecting differential solvation in H_2O and D_2O (free energy of transfer), is justified. In our treatment we show that this latter factor cannot be neglected, and that arbitrary superpositions of exchange and transfer effects—on any model—will fit the facts equally well.

The Gross–Butler model can best be tested when $k_H/k_D \approx 1$. Here, a bulge in H_2O/D_2O mixtures is predicted. There seems to be no experimental evidence for such a bulge. E. A. HALEVI, *Institute of Technology, Israel*

Reply: It is difficult to see how a treatment which predicts the dependence of the isotope effect on the solvent deuterium content for *any* protolytic reaction can fail to be general.

This general method of handling solvent isotope effects in H_2O/D_2O mixtures contains all the approximations inherent in the older derivations. In this sense it is not new. What is new, however, is the realization that there is a very simple correspondence between the chemical reaction to which the isotope effect refers and the equation relating the isotope effect to the solvent deuterium content. This new method of formulating these isotope effects eliminates the arduous algebraic manipulations which the older methods required. It permits predictions to be made for many more chemical reactions, and it clarifies the relationships between predictions for these systems.

This new method of predicting isotope effects does not neglect the free energy of transfer of solutes from H_2O to H_2O/D_2O mixtures any more than did previous treatments. Equation (16) in my paper contains activity coefficients for all solutes in both H_2O and H_2O/D_2O mixtures, and the ratio of any pair of these—the free energy of transfer for that species—can be handled just as Halevi, Long and Paul handled it in their treatment, or it can be treated in any other way. Thus, the method here does permit a superposition of exchange and transfer effects.

There is reason, however, to believe that transfer effects will usually be small. It is significant that a treatment which ignores transfer and uses a firmly established model of the solvated proton fits a good portion of the data. This is especially true for cases in which the observed value of the limiting isotope effect in D_2O makes the predicted isotope effects sensitive to the model used. (*cf. Figure 4*). KRESGE

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Comment: Dr Kresge has performed a valuable task in bringing together the formulations of protolytic equilibria in H_2O/D_2O mixtures for different assumptions about the numbers of equivalent hydrogen nuclei in the species involved in the reaction. It is a pity, however, that his use of unconventional symbols has made earlier equations assume an unfamiliar form.

It seems to me that Dr Kresge is unduly cautious about the extent of hydration of the hydrogen ion in aqueous solution. The case against the hydrogen's being an unhydrated proton now appears to be very strong. Halevi, Long and Paul described the model of a "non-specifically" solvated proton, but in calculations the non-specific solvation is not easily included. Evidence in favour of the formula L_3O^+ is provided by the variation of the ionic product of water in H_2O/D_2O mixtures, which is a particularly sensitive reaction for this purpose. Irrespective of the value assumed for the fractionation of deuterium between hydrogen ions and water, these results, which are given in a paper by Dr Lowe and myself (cited in Dr Kresge's paper as Reference 12), cannot simply be fitted by an unhydrated proton model, but they are well explained by a formula L_3O^+ for hydrogen ions. A second and more direct line of evidence is provided by measurements of isotope fractionation between hydrogen ions and water from chemical shifts of n.m.r. signals in solutions of strong mineral acids in H_2O/D_2O media rich in D. Such measurements have been carried out by Dr Lowe and myself (*loc. cit.*) and also by Drs Kresge and Allred (Dr Kresge's paper, reference 11). These results are again easily reconcilable with the formula L_3O^+ and incompatible with the formula L^+. V. GOLD, *University of London, England*

Reply: As regards symbols, Dr Gold must be referring to my use of x to represent the atom fraction of deuterium in the solvent. He prefers to use n, but we have already employed this letter to denote the number of water molecules associated with the proton in aqueous solution: $H^+(H_2O)_n$. Even though it now seems that this number can be fixed at unity in discussions of solvent isotope effects, it may have other values when it is measured by other methods†. It seems wise, therefore, to keep n for this purpose and to use another symbol to denote the atom fraction of deuterium in the solvent. We use x, which seems as good an alternative as any and is, in fact, often used to denote mole or atom fraction.

I agree with Dr Gold's statement that the unspecified solvation model for the proton in aqueous solution must now be rejected, and I would, in fact, like to endorse his reasons for accepting H_3O^+ as the model which should be used in connection with solvent isotope effects. There are now three recent and independent determinations of λ, the fractionation factor for the solvated proton. In two of these sets of experiments, which are cited in my paper as References 11 and 12, λ cannot be obtained from the primary data unless the model is specified—unless the n of $H^+(H_2O)_n$ is fixed. The third set of experiments, Gold's, was done at low acid concentration, and λ can be calculated to be the same for any reasonable value of n. Thus, two of these determinations of λ are model-dependent, whereas the third is model-independent. The only value of n for which the results of the former agree with that of the latter is unity. This seems to furnish very strong evidence for the H_3O^+ formulation. KRESGE

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Question: I should like to ask Dr Kresge if he applies the "law of the geometric mean" or something equivalent to it to transition-state concentrations. If so, would he comment on this use? M. WOLFSBERG, *Brookhaven National Laboratory, U.S.A.*

Answer: The statistical method which I developed for acid ionization equilibria is equivalent to applying the rule of the geometric mean, as shown in the first footnote to the section of my paper entitled "Derivation of a General Equation". Since my treatment of rates is simply an extension of this, the rule applies to transition-state concentrations as well. I cannot say now whether its application to kinetics is any less valid than its application to equilibria. KRESGE

Deuterium Solvent Isotope Effects on Acid–Base Equilibria in Dioxan–Water Mixtures—V. GOLD and B. M. LOWE, *University of London, England*

Comment: You draw the conclusion that the effect of dioxan on acid dissociation constants is mainly produced by a change in the activity of the undissociated acid. This would seem to be inconsistent if the effect is similar for water and acetic acid. V. J. SHINER, JR., *Indiana University, U.S.A.*

Reply: The same point is made in the final paragraphs of my paper. GOLD

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† E. Wicke, M. Eigen, and T. Ackermann. *Z. Physik. Chem.* **1**, 340 (1954).

Comment: The interesting results obtained by Dr Gold can be explained by the fact that the solvent is not homogeneous in the vicinity of the ions. The protons are, to a good approximation, in the form of hydrated H_3O^+. It is the difference in bonding in this species from that in the undissociated molecule which gives rise to the isotope effect k_H/k_D. We would expect the dioxan to have a 10 per cent effect on the hydrogen bonding in the water, as is the case with acetic acid. For the self-ionization of water the k_H/k_D ratio is larger than for acids because there is isotopic substitution in the OH^- ion. As a matter of fact, the k_H/k_D ratio for water ionization is small when account is taken of the fact that there are two protons replaced in the H_2O molecule. This is due to the fact that the OH^- has only one quantized motion for the proton.

The reason why dioxan has a larger effect, in the case of self-ionization, in water than in acetic acid is that the OH^- participates in the hydrogen bonding in water. The fact that this is destroyed by the dioxan results in a more pronounced influence on the k_H/k_D ratio. J. BIGELEISEN *Brookhaven National Laboratory, U.S.A.*

Comment: In the study of the autoprotolysis of water by Gold and Lowe $k_H/k_D = 7{\cdot}2$. This is a very large effect, and for such cases it was demonstrated in the paper by Long, Paul and myself that all the models display a qualitatively similar behaviour. To be sure, the experiments are in better accord with the Gross–Butler formulation than with any other single limiting model. E. A. HALEVI, *Institute of Technology, Israel*