The Prediction of Rate Constants from Equilibrium Data for Reactions in D2O–H2O Mixtures

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The five Raman lines near 2900 cm⁻¹ are undoubtedly to be assigned to the ν_H frequencies, together with the overtones of the δ_H frequencies, which will resonate with the 2900 cm⁻¹ fundamentals. The single infra-red band found at 2915 cm⁻¹ is probably an unresolved complex of several frequencies; the resolution of our instrument is quite low in this region.

With regard to the frequency of the torsional oscillations, γ, there is the interesting possibility that the Raman line at 300 cm⁻¹, if real, corresponds to this motion. Reliable information on this point, however, must await the complete vibrational analysis and accurate thermal data.

In concluding, we should like to express to Professor E. B. Wilson, Jr., our appreciation of the use of his laboratory, and of many helpful discussions during this work.

The Prediction of Rate Constants from Equilibrium Data for Reactions in D₂O-H₂O Mixtures

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The concentrations of hydrogen and deuterium ions at different fractions of D in the solvent are calculated from the simultaneous solution of the equations $C_{H^+} \cdot C_{HDO}/C_{D^+} \cdot C_{H_2O} = 3.76$ and $C_{H^+} + C_{D^+} =$ concentration of strong acid. Similarly, the concentrations of hydroxyl and deuteroxyl ions are calculated from the equations $C_{OD^-} \cdot C_{H_2O}/C_{OH^-} \cdot C_{HDO} = 0.225$ and $C_{OH^-} + C_{OD^-} =$ concentration of alkali. It is then possible to predict reaction rates for specific hydrogen ion and specific hydroxyl ion catalyzed reactions, in mixtures of $H_2O - D_2O$, on the assumption that the rate is proportional to the fraction of D^+ in the first case and to the fraction of OD^- in the second.

IT IS possible to predict the rate constant for specific hydrogen ion and hydroxyl ion catalyzed reactions in mixtures of deuterium and protium oxides from equilibrium data.

From the equilibrium equation[1]

$$K_1 = \frac{C_{H^+} \cdot C_{HDO}}{C_{D^+} \cdot C_{H_2O}} = 3.76 \qquad (1)$$

and from the equation

$$C_{D^+} + C_{H^+} = \text{Concentration of Strong Acid} \qquad (2)$$

TABLE I. *Concentration of H⁺, D⁺, OH⁻ and OD⁻ at different fractions of D in the solvent.*

F_D*	C_{H^+}	C_{D^+}	C_{OH^-}	C_{OD^-}
0.00	1.00	0.00	1.00	0.00
26.40	0.848	0.152	0.868	0.132
55.60	.627	.373	.665	.335
78.49	.376	.624	.417	.583
92.51	.152	.848	.175	.825
100.00	.00	1.00	.00	1.00

* $F_D = \Delta S(100)/0.1079 =$ Fraction of deuterium in the solvent.

[1] F. Brescia, J. Am. Chem. Soc. **60**, 2811 (1938).

in any $D_2O - H_2O$ mixture, the value of C_{H^+} and C_{D^+} can be calculated for different fractions of D in the solvent. The water concentrations, C_{HDO} and C_{H_2O}, are calculated from the equilibrium process[2] $H_2O + D_2O = 2HDO$ for which $K = 3.27$. A summary of the C_{H^+} and C_{D^+} values when the concentration of HCl is one molar is given in Table I.

The rate constant, k, at different fractions of D may then be calculated from these values of C_{H^+} and C_{D^+}, and from the values of the specific rate constant in ordinary water, k_{H^+}, and in $F_D = 100$ solvent, k_{D^+}, on the simple assumption that

$$k = k_{H^+} C_{H^+} + k_{D^+} C_{D^+}. \qquad (3)$$

This procedure was carried out for the reactions: the hydrolysis of acetal,[3] the hydrolysis of methyl acetate,[4] and the hydrolysis of ethyl

[2] B. Topley and H. Eyring, J. Chem. Phys. **2**, 217 (1934).
[3] W. J. C. Orr and J. A. V. Butler, J. Chem. Soc. (London) **1937**, 330.
[4] W. E. Nelson and J. A. V. Butler, J. Chem. Soc. (London) **1938**, 957.
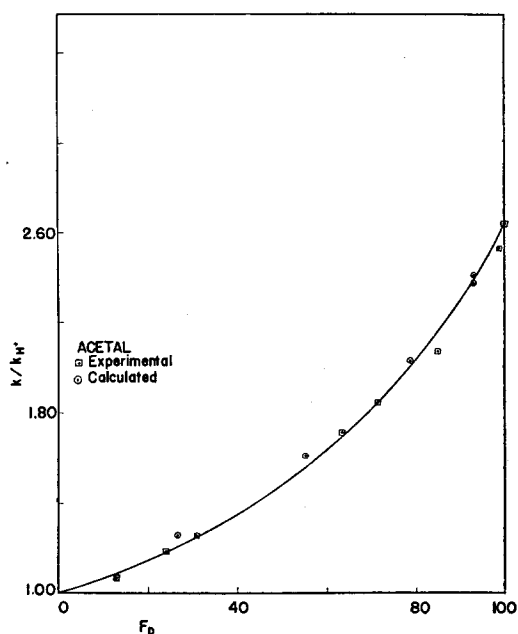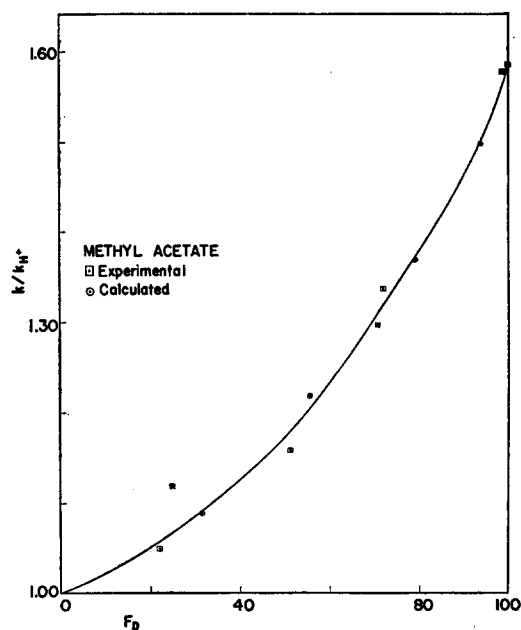
FIG. 1.

FIG. 2.

formate[4] which have been experimentally studied over a range of deuterium solvents. The values of k_{D^+} for the hydrolysis of ethyl formate and of methyl acetate reactions were extrapolated from the experimental data. In all other cases, the original author's extrapolated value for k_{D^+} was

TABLE II. *Summary of calculated and experimental values of k/k_{H^+}.*

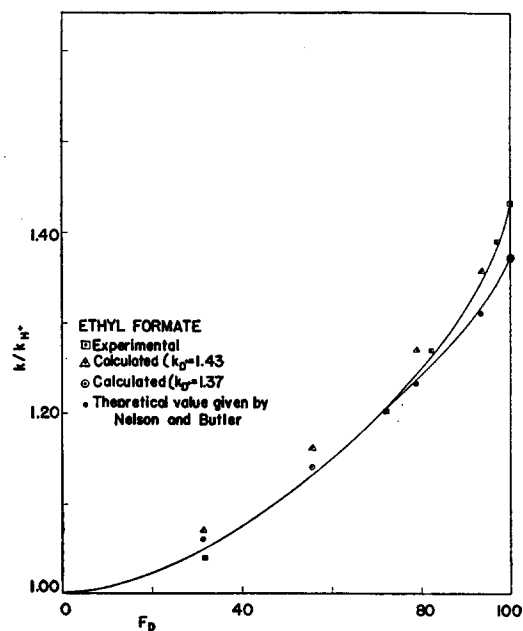| F_D	ACETAL		METHYL ACETATE		ETHYL FORMATE		
	EXP.[3]	CALC.	EXP.[4]	CALC.	EXP.[4]	CALC.	CALC.
0.00	1.00	(1.00)	1.00	(1.00)	1.00	(1.00)	(1.00)
12.4	1.074						
21.4			1.05				
24.1	1.19						
26.40		1.25		1.09		1.07	1.06
26.5			1.12				
27					1.04		
30.9	1.25						
51.2			1.16				
55.60		1.61		1.22		1.16	1.14
63.3	1.715						
70.3			1.30				
71.3	1.85		1.34				
72					1.20		
78.49		2.03		1.37		1.27	1.23
82					1.27		
84.8	2.08						
92.51		2.39		1.50		1.36	1.31
96					1.39		
98.4			1.58				
98.5	2.51?						
100.0	(2.64)	(2.64)	(1.59)	(1.59)	(1.43)	(1.43)	(1.37)

FIG. 3.

used. The experimental data and calculated values are summarized in Table II and plotted in Figs. 1, 2 and 3. In each case, the agreement between the calculated and the measured rate is within the experimental error. It should be noted in the case of ethyl formate that "considerable difficulty was experienced in obtaining stable
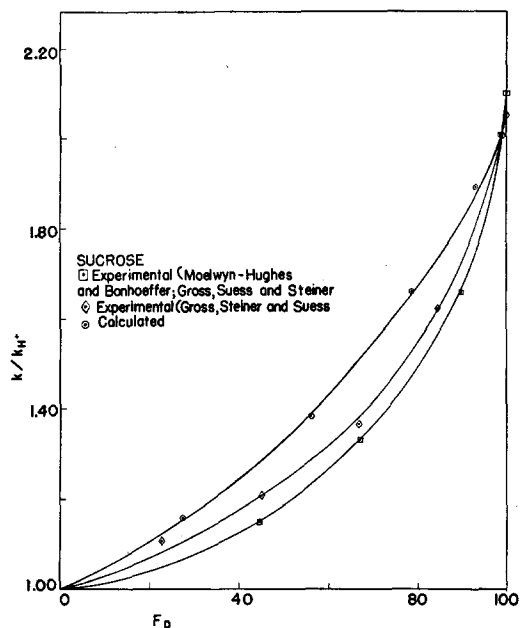
FIG. 4.

final readings and the accuracy of the series is not great."[4] If the theoretical value (1.37), given by Nelson and Butler,[4] for the k_{D^+} for the ethyl formate reaction is used, better agreement is obtained.

The same procedure applied to the sucrose inversion in $H_2O - D_2O$ mixtures does not yield results in agreement with the available experimental data[5] which, in itself, is not consistent. In the mutarotation of glucose reaction, which is exceptional in that the k_{D^+} is smaller than the k_{H^+}, the theoretical curve shows a positive deviation from linearity whereas the best curve through the experimental data[6] is a straight line. The calculated and experimental results for these reactions are given in Table III and plotted in Figs. 4 and 5.

This method is analogous in principle to that employed by Hamill and La Mer[7] except that they used the equilibrium equation

$$\frac{C_{D_2O} \cdot C^2_{H^+}}{C_{H_2O} \cdot C^2_{D^+}} = 15.7 \tag{4}$$

calculated by Korman and La Mer[8] from electromotive force data whereas the equation

$$\frac{C_{H^+} \cdot C_{HDO}}{C_{D^+} \cdot C_{H_2O}} = 3.76 \tag{1}$$

has been independently calculated from kinetic measurements.

The derivation of a value for the equilibrium constant for the process

$$OH^- + HDO = H_2O + OD^- \tag{5}$$

permits the similar calculation of the rate constant for a specific hydroxyl ion catalyzed reaction in mixtures of D and H waters. This is now accomplished as follows. The equilibrium constants of the following processes are known:[1, 2, 9]

$$D_2O = D^+ + OD^-; \quad K_{DW} = \frac{1.95 \times 10^{-15}}{55.15}, \tag{6}$$

$$H_2O = H^+ + OH^-; \quad K_{HW} = \frac{10^{-14}}{55.33}, \tag{7}$$

$$D^+ + H_2O = H^+ + HDO; \quad K_8 = 3.76, \tag{8}$$

$$D_2O + H_2O = 2HDO; \quad K_9 = 3.27. \tag{9}$$

FIG. 5.

[5] (a) E. A. Moelwyn-Hughes and K. F. Bonhoeffer, Naturwiss. 22, 174 (1934); P. Gross, H. Suess and H. Steiner, ibid. 22, 662 (1934); (b) P. Gross, H. Steiner and H. Suess, Trans. Faraday Soc. 32, 883 (1936).

[6] W. H. Hamill and V. K. La Mer, J. Chem. Phys. 4, 395 (1936).

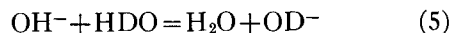[7] W. H. Hamill and V. K. La Mer, J. Chem. Phys. 4, 294 (1936).
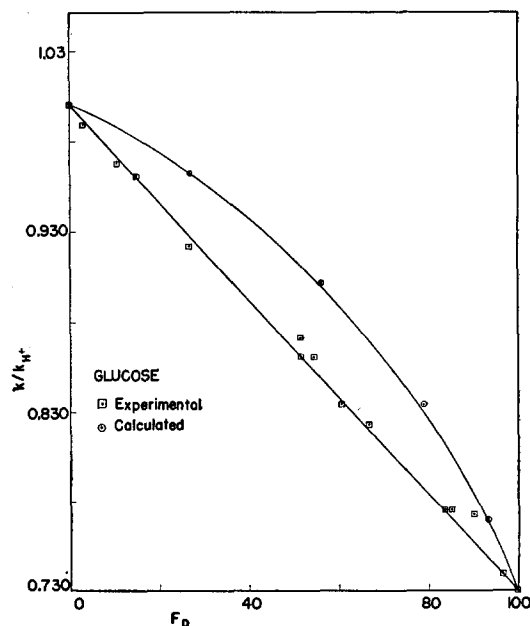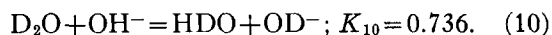
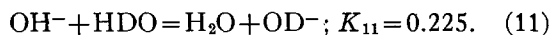[8] S. Korman and V. K. La Mer, J. Am. Chem. Soc. 58, 1396 (1936).

[9] W. F. K. Wynne-Jones, Trans. Faraday Soc. 32, 1397 (1936).

Subtracting (7) from (6) and adding (8) yields

$$D_2O + OH^- = HDO + OD^-; \quad K_{10} = 0.736. \quad (10)$$

Subtracting (9) from (10) yields

$$OH^- + HDO = H_2O + OD^-; \quad K_{11} = 0.225. \quad (11)$$

Doubling (10) and subtracting (9) yields

$$D_2O + 2OH^- = H_2O + 2OD^-; \quad K_{12} = 0.166. \quad (12)$$

The value for K_{12} is much lower than the value, 0.413, calculated by Korman and La Mer[8] from electromotive force measurements.

From the value of the equilibrium Eq. (11) and from the equation

$$C_{OH^-} + C_{OD^-} = \text{Concentration of Alkali} \quad (13)$$

in any $D_2O - H_2O$ mixture, the values of C_{OD^-} and C_{OH^-} can be calculated at different fractions of D in the solvent. A summary of these values when the concentration of alkali is one molar is given in Table I.

On the analogous assumption that

$$k = k_{OH^-} C_{OH^-} + k_{OD^-} C_{OD^-}, \quad (14)$$

where k_{OH^-} and k_{OD^-} are the specific rate constants in $F_D = 0$ and $F_D = 100$ solvent, the rate
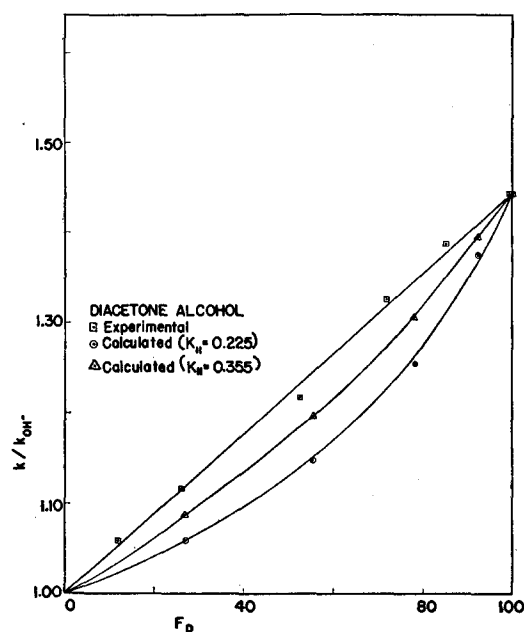

FIG. 6.

constant, k, at different fractions of D may be calculated. This was done for the decomposition of diacetone alcohol[4] and the results (Table III) are in very poor agreement with the experimental curve (Fig. 6). On the other hand, if the value of K_{11} is calculated from Korman and La Mer's value for K_{12} and from K_9, it is found to be 0.355 instead of 0.225. Repetition of the calculation of k based on the value 0.355 for K_{11} yields results (Table III, Fig. 6) very close to the experimental data. A slight but definite sag in the curve is observed whereas the available data indicates a straight line relation between k and F_D.

The predicted rates are in good agreement, on the whole, with the available experimental rates for specific hydrogen ion catalyzed reactions in which the rate is faster in D_2O. It is difficult to draw conclusions for the base catalyzed reaction since only one set of experimental data is available for comparison. It is quite possible that the lack of agreement in the sucrose, glucose and diacetone alcohol reactions may be due to substrate exchange with solvent. Preliminary results[10] seems to indicate the possibility that the rate of the base catalyzed reaction of nitramide decomposition is a linear function of F_D. Nitramide also exchanges with the solvent.

TABLE III. *Summary of calculated and experimental values of k/k_{H^+} and k/k_{OH^-}.*

F_D	Sucrose, k/k_{H^+}			Glucose, k/k_{H^+}		Diacetone Alcohol, k/k_{OH^-}		
	Exp.[5a]	Exp.[5b]	Calc.	Exp.[6]	Calc.	Exp.[4]	Calc.[*]	Calc.[†]
0.00	1.00	1.00	(1.00)	1.00	(1.00)	1.00	(1.00)	(1.00)
3.5				0.987				
10.8				.965				
12.1						1.06		
14.5				.958				
22.5		1.11						
25.9						1.12		
26.40			1.16		0.959		1.06	1.09
26.5				.920				
44.4	1.15							
44.7		1.21						
50.7				.871				
51.				.859				
52.9						1.22		
54.				.859				
55.60			1.39		.899		1.15	1.20
60.				.833				
66.3				.823				
66.6		1.37						
67.1	1.33							
72.5						1.33		
78.49			1.66		.832		1.26	1.31
83.1				.775				
84.				.775				
84.2		1.63						
85.3						1.39		
89.				.772				
90.	1.66							
92.51			1.89		.771		1.38	1.40
96.				.740				
98.1	2.01							
98.4		2.01						
99.						1.44		
99.6						1.45		
100.0	(2.10)	(2.05)	(2.05)	(0.730)	(0.730)	(1.45)	(1.45)	(1.45)

* Calculations based on $K_{11} = 0.225$.
† Calculations based on $K_{11} = 0.355$.

[10] S. Hochberg and V. K. La Mer, unpublished.