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Thermodynamics and Kinetics of the Gas-Phase Reactions: $H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n$

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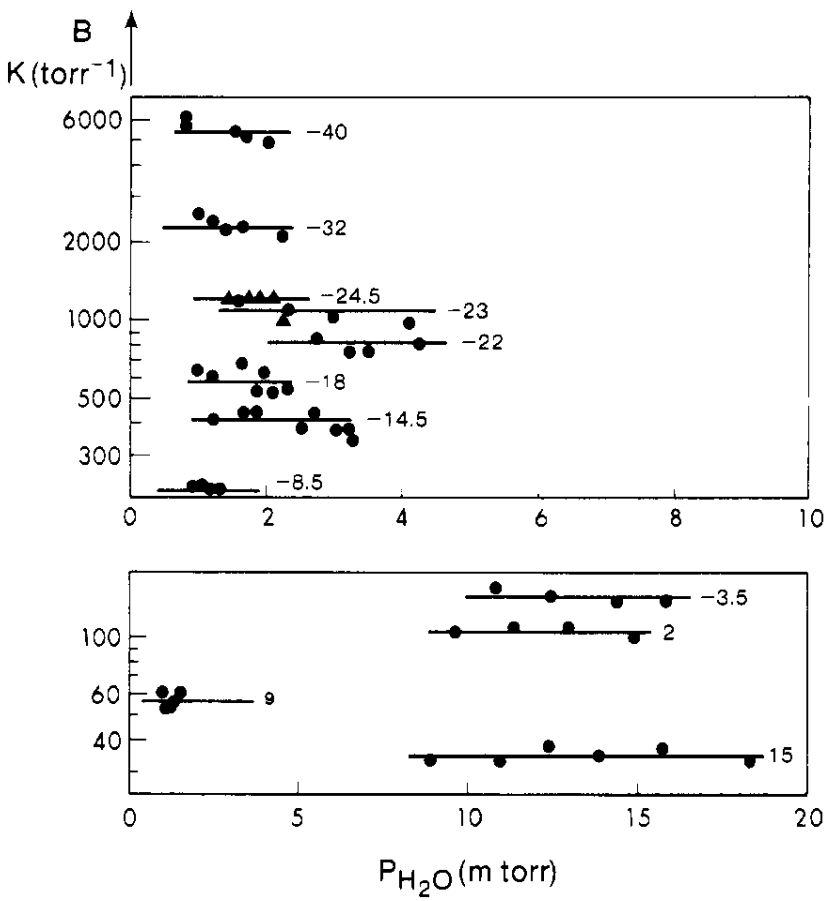

Figure 1. (*A*,*B*) Measured equilibrium constant $K = K_{3,4}$ for the equilibrium $H_3O^+(H_2O)_3 + H_2O = H_3O^+(H_2O)_4$. Mixtures of the major gas methane containing the partial pressures of water shown on the abscissa were used. The points for one given determination in the figure were generally obtained by using a constant methane to water ratio and changing the total ion source pressure. The water partial pressure range shown in the figure generally corresponds to a total ion source pressure range from 0.8 to 2.5 Torr. Numbers beside straight lines give temperature in degrees C.

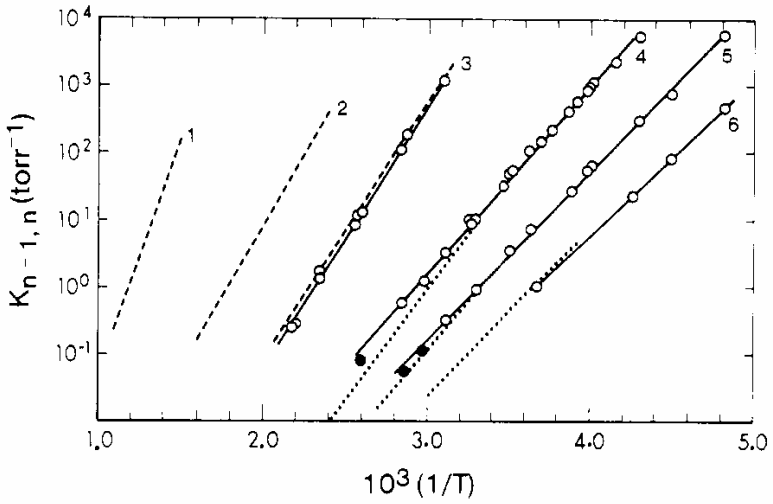

Figure 2. van't Hoff plots of equilibrium constants $K_{n-1,n}$ for reactions $(n-1,,n)$ $H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n$: present results (—), Cunningham et al.[11] (- - -), Searles et al.[10] (···). All data points are from present work: (○) major gas CH_4, (●) neat H_2O. Plots of Cunningham and Searles are shown over the exact temperature range used in respective experiments. Present data are in good agreement with the Cunningham (2,3) plot. Cunningham (0,1), (1,,2), and (2,3) plots plus present data for $(n-1,n)$ are the "best set" of determinations for the reactions $(n-1,n)$ from this laboratory.

Table I. Data for the Equilibria: $H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n$[a]

$(n-1,n)$	$-\Delta H^\circ_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$	$-\Delta G^\circ_{n-1,n}$(300 K)	$-\Delta H^\circ_{n-1,n}$[d]	$-\Delta E_{n-1,n}$[e]
0,1	31.6[b] (36)[c]	24.3[b]	24.3 (25)[c]	33.0	37
1,2	19.5[b] (22)[c]	21.7[b]	13.0 (13.6)[c]	21.0	26
2,3	17.9 (17)[c]	28.4	9.5 (8.5)[c]	16.0	22
3,4	12.7 (15)[c]	23.4	5.6 (5.5)[c]	14.8	16
4,5	11.6 (13)[c]	25.0	4.1 (3.9)[c]		15
5,6	10.7 (12)[c]	26.1	3.0 (2.8)[c]		
6,7	(10)[c]				

[a] ΔH°, ΔG° in kcal mol^{-1}, ΔS° in cal K^{-1} mol^{-1}. Standard state 1 atm. Data in parentheses are previous data from this laboratory which are of lower accuracy than unparenthesized results from this laboratory. [b] Cunningham.[11] [c] Searles.[10] [d] Meot-Ner[12] equilibria measurements. [e] Newton[19] 4-31G calculated energies with zeropoint correction.