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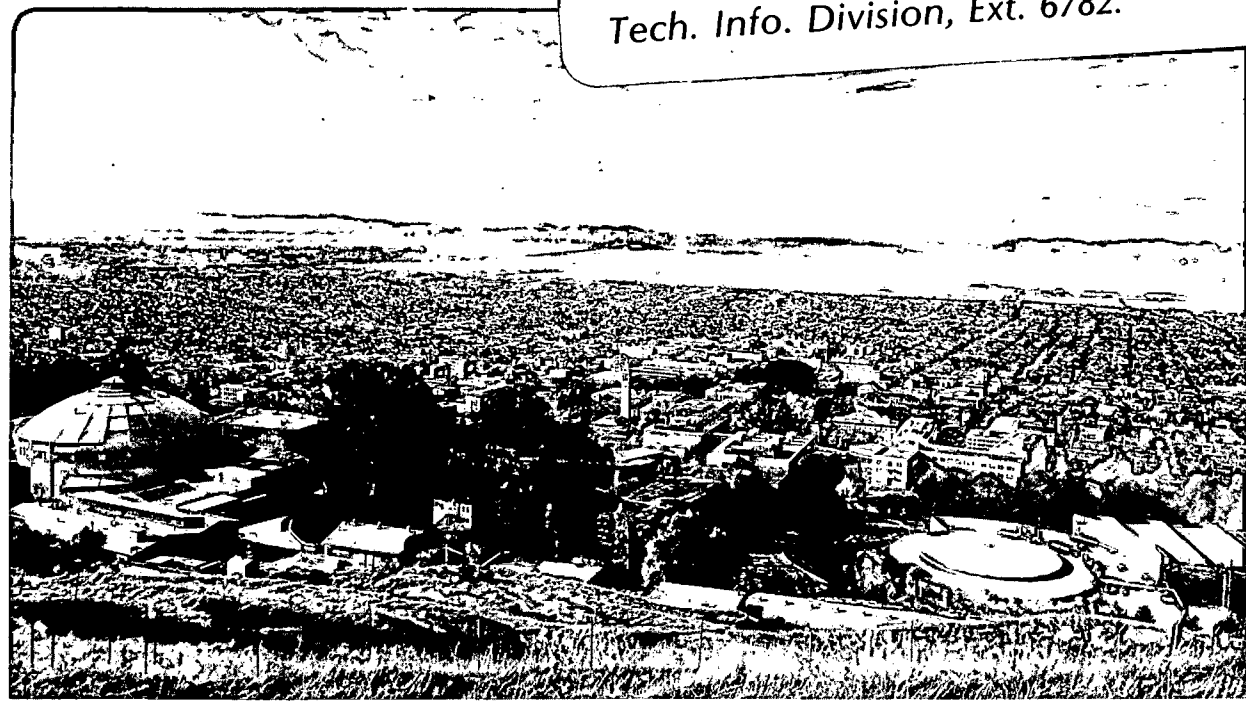
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May 1982

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Self-Ionization of Water at High Temperature
and the Thermodynamic Properties of the Ions

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Abstract

It is shown that gas phase data on hydrated H^+ and OH^- ions from mass spectrometry can be used to calculate the ionization product for water at high temperature and at high enough pressure to allow relating these results with those directly measured near 1000 K and 0.5 gm cm^{-3} . The thermodynamic properties of the hydrated H^+ and OH^- are discussed and the heat capacity is compared with results calculated from the Born equation for an appropriate region of temperature and pressure.

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, Mathematics, and Geosciences of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

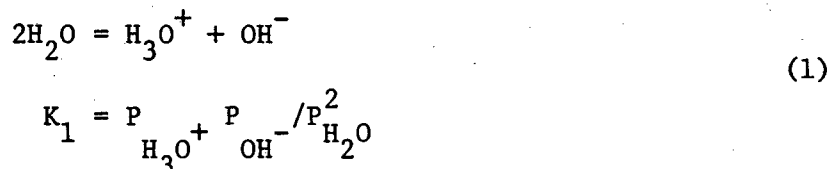
The ionization product for water has been investigated over a wide range of temperature, and Marshall and Franck¹ have recently proposed an empirical equation after a careful review of the various direct measurements. This equation appears to be an excellent representation of these data which are for densities above 0.4 g cm^{-3} . It is interesting to consider the behavior of the ionization product at lower density than 0.4 in the range near or above the critical temperature. The Marshall and Franck equation can be extrapolated into this region; indeed Gates, Wood, and Quint² have used such extrapolated values to discuss the behavior of the partial molal heat capacity of ions near the critical point. But long extrapolations are dangerous. In this paper the properties of gaseous, water-related ions³ are used to calculate the ion product for steam. These results appear to be valid at pressures gradually increasing with temperature until the curve can be connected with the directly measured experimental values of Quist⁴ at 1073 K and 0.5 g cm^{-3} . At lower temperatures one can interpolate between these newly calculated curves at lower density and the equation of Marshall and Franck for the high density region. These interpolated curves, although still somewhat uncertain, should be much more reliable than extrapolations considering only the high-density data.

The thermodynamic properties, including the partial molal heat capacities, of the ions can be calculated from the ion product equation. These properties are discussed in comparison with calculations from the Born equation and the earlier results of Gates, et al.²

Gaseous Ion Equilibria

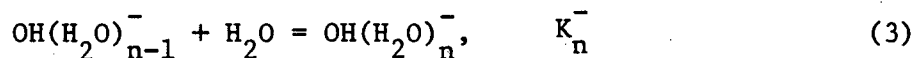
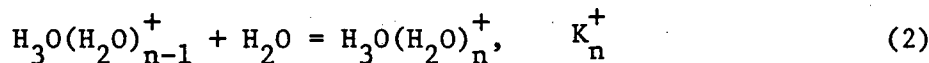
The thermodynamic properties of gaseous H^+ and OH^- and their hydrated ions are known. The equilibria between the successive hydrate ions were measured, primarily by Kebarle and his associates,^{3,5-7} with a mass

spectrometer having a relatively high pressure of H_2O in the ion source. The first hydration of the proton is complete under all conditions of present interest, hence we consider as the initial reaction



for which^{3,8} $\Delta H_0^\circ = 222 \text{ kcal mol}^{-1}$. The partition function product for H_3O^+ and OH^- should be almost exactly the same as that for NH_3 and HF which can be found, as $-(G^\circ - H_0^\circ/RT)$, in appropriate tables.⁹ Thus one has the equilibrium constant K_1 for reaction (1).

But with increasing pressure of H_2O most of these ions are further hydrated



with equilibrium constants K_n^+ and K_n^- . Table 1 gives the values of ΔH_n° and ΔS_n° which are derived from these measured equilibria. Also listed are the approximate temperatures T_n^* where the equilibria were measured.

For our purpose we need the sum of the partial pressures of all hydrates of H^+ and the corresponding sum for OH^- . We write

$$\frac{\Sigma P_n^+}{P_{H_3O^+}} = (S^+) = [1 + K_1^+ P_{H_2O} + K_1^+ K_2^+ P_{H_2O}^2 + \dots] \quad (4)$$

$$\frac{\Sigma P_n^-}{P_{OH^-}} = (S^-) = [1 + K_1^- P_{H_2O} + K_1^- K_2^- P_{H_2O}^2 + \dots] \quad (5)$$

where the reasons for these definitions will be apparent later. While, at low pressure only the first few hydrates are significant, under higher pressures

most of the ions are highly hydrated. Thus a model is needed for hydration equilibria of indefinite order. The expressions labeled A in Table 1 for $n \geq 4$ represent quite accurately the measured values for n from 4 through 6 for positive ions⁵ and through 5 for negative ions.^{3,6-7} Eventually the rate of reduction of $-\Delta H_n$ for successive values of n will undoubtedly decrease well below the increment of 1 kcal mol^{-1} given for expression A. Hence, as an alternate model B, this quantity is decreased to $0.8 \text{ kcal mol}^{-1}$. For any given T and P , if models A and B give the same result, it should be reliable; if they differ slightly, the result for A should be preferred and reliable; while if they differ somewhat more, the correct result should lie between those for A and B. With increasing difference, i.e., very high order of hydration, the correct result may lie on either side of that for model B which should be better than A. Eventually as P increases, this treatment based on gas phase equilibria will become unsatisfactory and this is indicated by a gross difference between the results from models A and B as well as by substantial departures of the properties of the steam from the ideal gas equation.

Also to be considered is the value of ΔC_p for the successive hydration equilibria. This quantity was neglected in evaluating the mass spectrometric data over a limited range of temperature for a given n . But we will be extrapolating values for the higher n 's from near or below room temperature to above 1000 K. Hence a nonzero ΔC_p should be considered for use from the T_n^* of measurement to the T of interest. A hydration reaction converts 3 modes of translation and 3 of rotation to six low frequency vibrational modes in the larger cluster. The torsional modes, especially, will be quite anharmonic. Also one PV term will be lost. Hence we expect ΔC_p to be given by $6(R+?) - 4R$ or substantially in excess of $2R$. Alternate exploratory calculations were made for $\Delta C_p = 3R$ and $4R$. The final calculations take $\Delta C_p = 3.5 R$.

The conventional definition of K_w is the product of the molalities of H^+ and OH^- representing the sums of species of all degrees of hydration in each case. The molality, in turn, is the ratio of moles of solute Σn^+ , Σn^- to kg of water w_{H_2O} . Hence

$$K_w = \frac{m_{H^+} m_{OH^-}}{m_0^2} = \frac{(\Sigma n^+)(\Sigma n^-)}{m_0^2 w_{H_2O}^2} \quad (6)$$

$$= \left(\frac{n_{H_2O}}{m_0 w_{H_2O}} \right)^2 \left[\frac{(\Sigma n^+)(\Sigma n^-)}{n_{H_2O}^2} \right]$$

where $m_0 = 1 \text{ mol kg}^{-1}$ is introduced to make K_w dimensionless. The quantity $(n_{H_2O}/m_0 w_{H_2O})$ is 55.5. The mole ratios in brackets are equal to the corresponding ratios of partial pressures which are used for the gas phase equilibria. Thus, we can substitute from equations (1), (4), and (5) and obtain

$$K_w = (55.5)^2 K_1(S^+)(S^-). \quad (7)$$

In presenting the results it is desirable first to seek a most meaningful comparison between the values from these calculations with those from conventional experiments which are mostly for liquid-like conditions. The best conditions for comparison will be at the highest temperature and lowest density of accurate measurement. The highest temperature of Quist's measurements⁴ is 1073 K and his data extend in density from 0.65 to 0.50 g cm^{-3} at that temperature. While steam at these conditions is too non-ideal for an accurate direct comparison, the gap is not very large as is seen on figure 1. An essentially unambiguous smooth curve connects the calculated points at lower density with Quist's experimental points. While both the experiments and the

calculations are subject to appreciable uncertainty, it seems clear that the solid curve for 1073 K is essentially correct.

More particularly, where two points are shown on figure 1 the upper is based on model B and the lower on model A as defined above and in Table 1. The initial calculations for $\Delta C_p = 3 R$ and $4 R$ both allowed reasonable curves to be extended through the high density data of Quist. Thus the intermediate value $\Delta C_p = 3.5 R$ seemed to be the best choice both on the basis of consistency with the high-density experimental data and the theoretical considerations stated above. The curve for 1073 K passes through the points for model A except for the widely separated points at $\log \rho = -0.6$ where it passes between the pair of points.

The straight, dashed line shows the extrapolation of the Marshall and Franck¹ equation. While qualitatively correct in indicating a rapid decrease in K_w with decrease in density, that line departs considerably from our calculated curve in the range of $\log \rho$ near -1 and then, after a crossing, has a totally different trend at low densities.

The corresponding data for 873 K are also shown on figure 1 while those for 673 K are on figure 2. At 873 K the range for interpolation (shown dashed) between experimental data at high densities and reliable calculations for low densities is not wide, but a more complex curve with two inflexions is required in this region. The location of this interpolating curve, however, is quite unambiguous. At 673 K the range for interpolation is much wider and reasonable curves can be drawn which differ appreciably in their prediction of $\log K_w$ near $\log \rho = -1$.

Figure 3 gives curves at constant pressures of 50, 100, and 221 bar, the last being the critical pressure. The curve from the Marshall and Franck equation for 221 bar is also shown and is accepted for the liquid below the

critical temperature. But above T_c our calculations indicate that K_w becomes much smaller than the values of Marshall and Franck,¹ by about 8 powers of ten near 800 K.

Calculations were also made for somewhat lower temperatures, 613, 633, and 653 K. In this range K_w is very small indeed at moderate pressure; for example at 613 K, $\log K_w = -60.6$ at 1 bar and -52 at 10 bar. These values correspond to a single pair of substantially hydrated H^+ and OH^- ions in 3×10^6 kg and in 200 kg of steam, respectively. At 50 bar Marshall and Franck¹ give extrapolated values of about -33 in this temperature range whereas our calculations indicate values near -43 or 10 powers of ten smaller for K_w . The ions are highly hydrated under these conditions; hence our calculated values also involve extrapolation of the experimental data to higher order of hydration. Direct experiments appear to be almost impossible for conditions where there is so little ionization.

While the figures probably present the results with the precision justified by the uncertainties of the experiments and the additional assumptions in the calculations, tables of calculated values are available in the Appendix together with additional details of the calculations.

Discussion

The mass spectrometric data of Kebarle and associates^{3,5,6} give a detailed picture of the thermodynamics of ion hydration. Nevertheless, it is also interesting to consider the overall effects, i.e., the partial molal properties of ions at infinite dilution in water as a function of temperature and pressure. The Gibbs energy, enthalpy, and heat capacity below the critical pressure have been measured and discussed by various workers. The heat capacity and the enthalpy both approach negative infinity as T approaches T_c from

below. Gates, et al.,² discuss this behavior and the various sources of evidence. They also show that the Born equation predicts this same pattern of behavior on the very reasonable assumption that $(\partial D/\partial \rho)_T$ remains positive and finite in the critical region where $(\partial \rho/\partial T)_P$ becomes negative infinity. Thus $(\partial D/\partial T)_P$ also approaches negative infinity.

Consideration of the second derivatives which appear in the equations for the heat capacity indicate that this quantity approaches positive infinity as T approaches T_c from above. Gates, et al., demonstrate this in detail and compare the curve given by extrapolation of the Marshall and Franck equation into this region with that for the Born equation. They find this qualitative pattern in both cases.

For their Born equation calculations, Gates, et al.,² assume a Born radius of 0.2285 nm to fit the experimental or slightly extrapolated results for $\bar{C}_{p,2}^\circ$ of the ions in the liquid below T_c . They find substantial differences between values from the Born equation and those from the extrapolated Marshall and Franck¹ equation above T_c at $P_c = 221$ bar, and they assume that the latter are more nearly correct. From figure 3 it is apparent that reliable values of $\log K_w$ can be calculated from gas phase data above about 850 K and that the true curve probably lies much lower than that extrapolated from Marshall and Franck in the region from T_c to 850 K. Table II gives values of $\bar{C}_{p,2}^\circ$ based on the calculated and interpolated curve of figure 3 for comparison with those given by Gates, et al.² These results suggest strongly that the Born equation gives an excellent approximation to the true behavior in the region significantly above T_c at P_c . Thus there is no need to discuss reasons for inaccuracy of the Born equation in this region; rather one remarks that the Born equation appears to be remarkably accurate even when the effective radius was fitted to data at much lower temperature.

In this region above T_c , the large positive heat capacity arises from the absorption of energy to dissociate water molecules from the clusters around the ions. The average n for clusters near T_c is large, but by 1000 K at P_c the average n is considerably reduced. This is shown by the near equality of the values from model A and model B at 973 K and especially at 1073 K and was verified by separate calculations which yield an average n near 7 at 1000 K and P_c .

It should also be recognized that the primary objective of Marshall and Franck¹ was an equation for K_w for the region where the dissociation is sufficiently large to be of interest in connection with steam boilers and similar practical situations. From this point of view it is of little consequence that K_w is even smaller in regions where their equation predicts an extremely small value.

Acknowledgments

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, Mathematics, and Geosciences of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. The writer thanks Professor R. H. Wood for a copy of his paper with Gates and Quint in advance of publication.

Appendix

Table A1 gives the values of $-\log K_1$ while Tables A2 and A3 give values of $-\log K_w$ calculated from the parameters in Table I with $\Delta C_p = 3.5 R$. Values for models A and B are indicated by those letters.

In Table I the values for the positive ions were taken from Lau, Ikuta and Kebarle.⁵ For the negative ions the case is less clear; there are differences between later reviews and the original values of Arshadi and Kebarle⁶ or Payzant, et al. Values from the 1977 review³ were chosen in most cases. The differences are not large.

The calculations could be refined by use of fugacities instead of partial pressures, but the differences would be smaller than the uncertainties related to ΔC_p and to some of the parameters in Table I. Since ΔC_p was, in a sense, adjusted to optimize the fit with the high-density data of Quist, the refinement of fugacity coefficients seemed inappropriate. Debye-Hückel effects were considered and found to be negligible for the very small ionic strengths involved. Also K_w is strictly defined in terms of activity rather than molality. Thus the effect of an activity (or fugacity) coefficient less than unity for all ions would be to increase the concentration of ions but to leave the activity product and K_w unchanged.

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TABLE I. Enthalpy and Entropy Changes^a for Successive Hydration of H_3O^+ and OH^-

n	T*/K	$\frac{-\Delta S_{T^*}^\circ}{\text{cal K}^{-1} \text{ mol}^{-1}}$	$\frac{-\Delta H_{T^*}^\circ}{\text{kcal mol}^{-1}}$	Model
(positive ions)				
1	700	24.3	31.6	
2	500	21.7	19.5	
3	380	28.4	17.9	
4+	250	25.0	$\left\{ \begin{array}{l} 13.0 - (n-4) \\ 13.0 - 0.8(n-4) \end{array} \right.$	A
				B
(negative ions)				
1	600	20.8	25.0	
2	500	21.	17.9	
3	400	25.	15.	
4+	330	25.	$\left\{ \begin{array}{l} 14. - (n-4) \\ 14. - 0.8(n-4) \end{array} \right.$	A
				B

^a Values from references 3, 5, 6, and 7.

TABLE II. The Partial Molal Heat Capacity of Ions at the Critical Pressure and above T_c

$\frac{T}{K}$	$C_{p,2}^{\circ}/R$		
	This Research	Born Eq.	Extrapolated M.F.
700	1400	1900	450
750	600	650	120
800	350	350	50
1000	70	88	-2

TABLE A1. Values for $\log K_1$

T/K	$-\log K_1$
613	79.5 ₉
633	77.1 ₀
653	74.7 ₅
673	72.5 ₄
773	63.2 ₃
873	56.0 ₇
973	50.3 ₈
1073	45.7 ₃

TABLE A2. Values of $-\log K_w$ for Models A and B as Indicated

P/bar	Model	673	773	873	973	1073 K
1	A,B	57.1	51.8	47.3	43.3	39.9
3	A,B	54.5	49.8	45.5	41.8	38.7
10	A	50.4	46.9	43.2	39.9	36.9
10	B	50.3	46.9	43.2	39.9	36.9
30	A	45.4	43.0	40.3	37.5	34.9
30	B	44.8	42.8	40.3	37.5	34.9
50	A	42.5	40.7	38.4	36.1	33.7
50	B	41.6	40.3	38.3	36.0	33.7
100	A	38.2	37.0	35.3	33.4	31.5
100	B	36.7	36.2	34.9	33.2	31.4
300	A	30.2	29.7	28.8	27.6	26.2
300	B	27.6	28.0	27.6	26.7	25.6
1000	A	-	-	19.6	18.8	17.9
1000	B	-	-	17.0	16.7	16.1

TABLE A3. Additional Values of $-\log K_w$ for Models A and B as Indicated

P/bar	613 A	613 B	633 A	633 B	653 A	653 K B
1	60.6	60.6	59.5	59.5	58.3	58.3
3	57.3	57.2	56.4	56.3	55.5	55.4
10	52.3	51.9	51.8	51.4	51.1	50.9
30	46.5	45.4	46.2	45.3	45.8	45.1
50	43.3	41.9	43.1	41.9	42.9	41.8
100	38.6	36.5	38.5	36.7	38.4	36.7
221	-	-	-	-	32.6	30.1

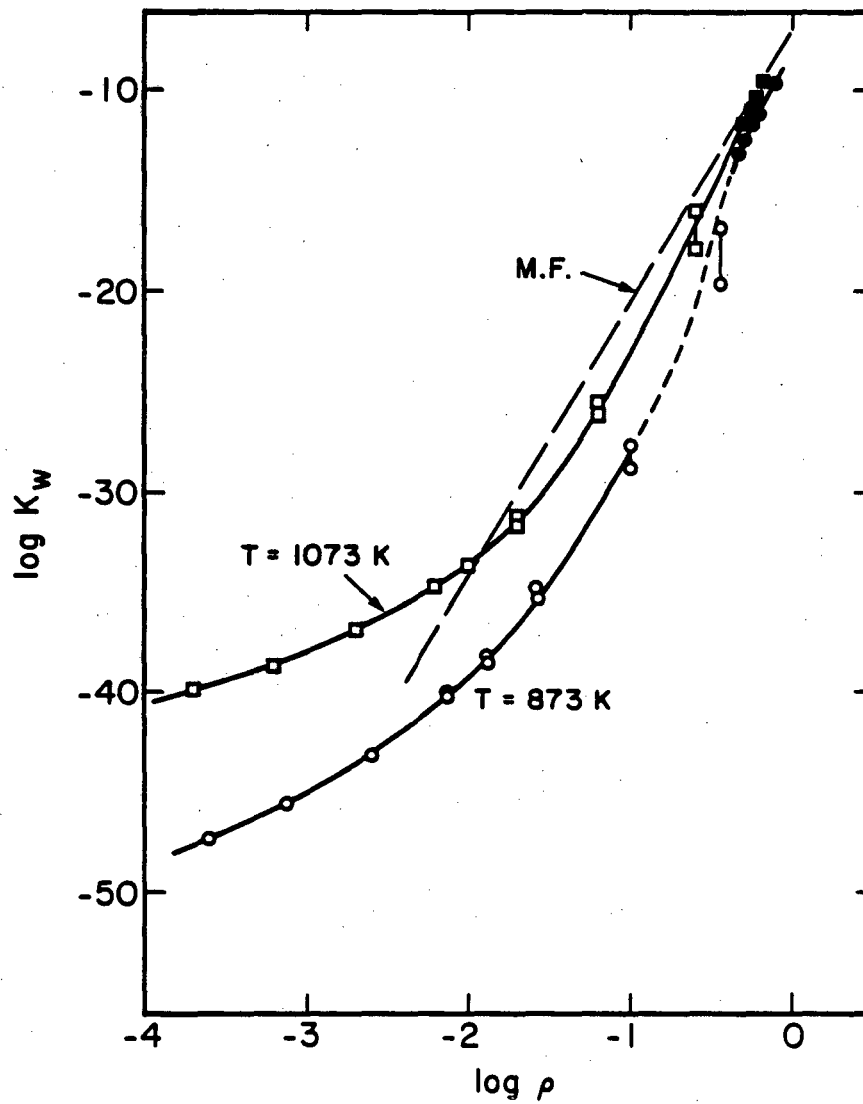


Figure 1. The ionization product for water K_w as a function of density at very high temperature. Solid symbols show experimental values from Quist;⁴ open symbols show calculated values. The line marked M.F. is from Marshall and Franck.¹

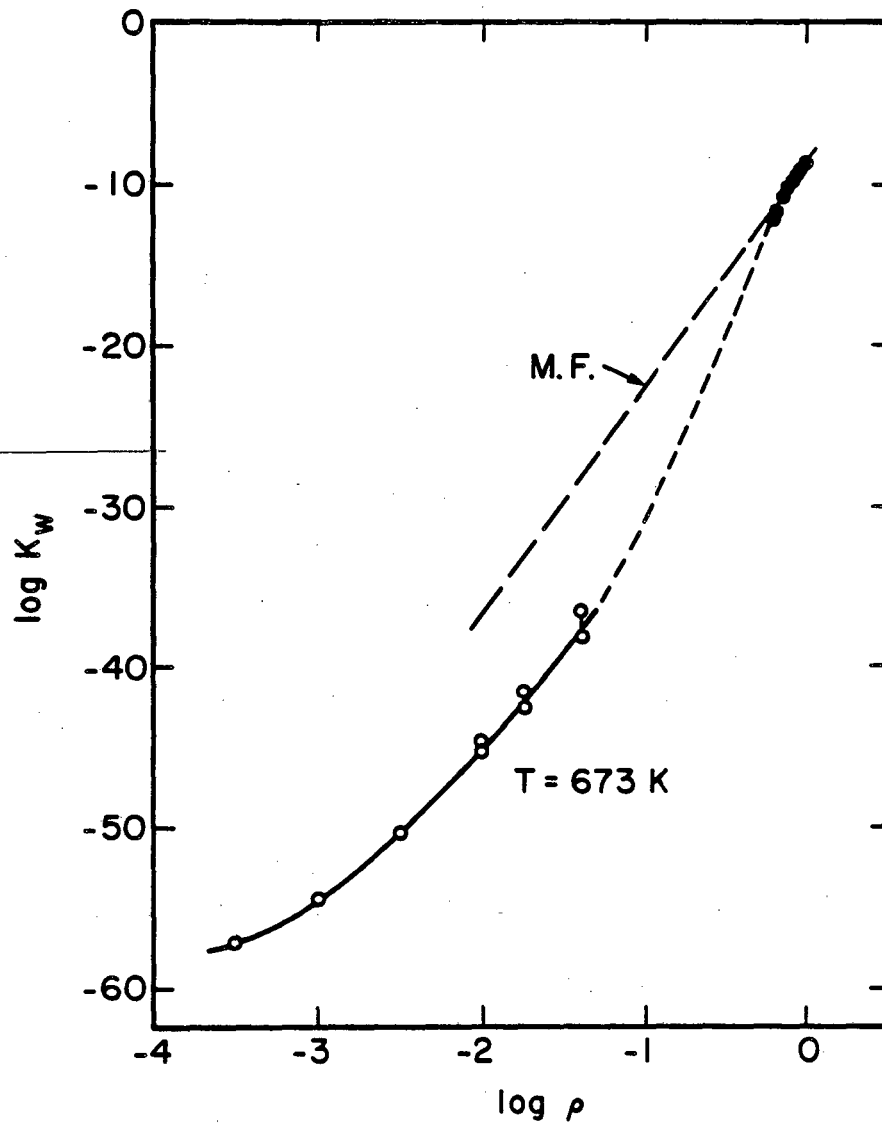


Figure 2. The ionization product at intermediate temperature; details are the same as for figure 1.

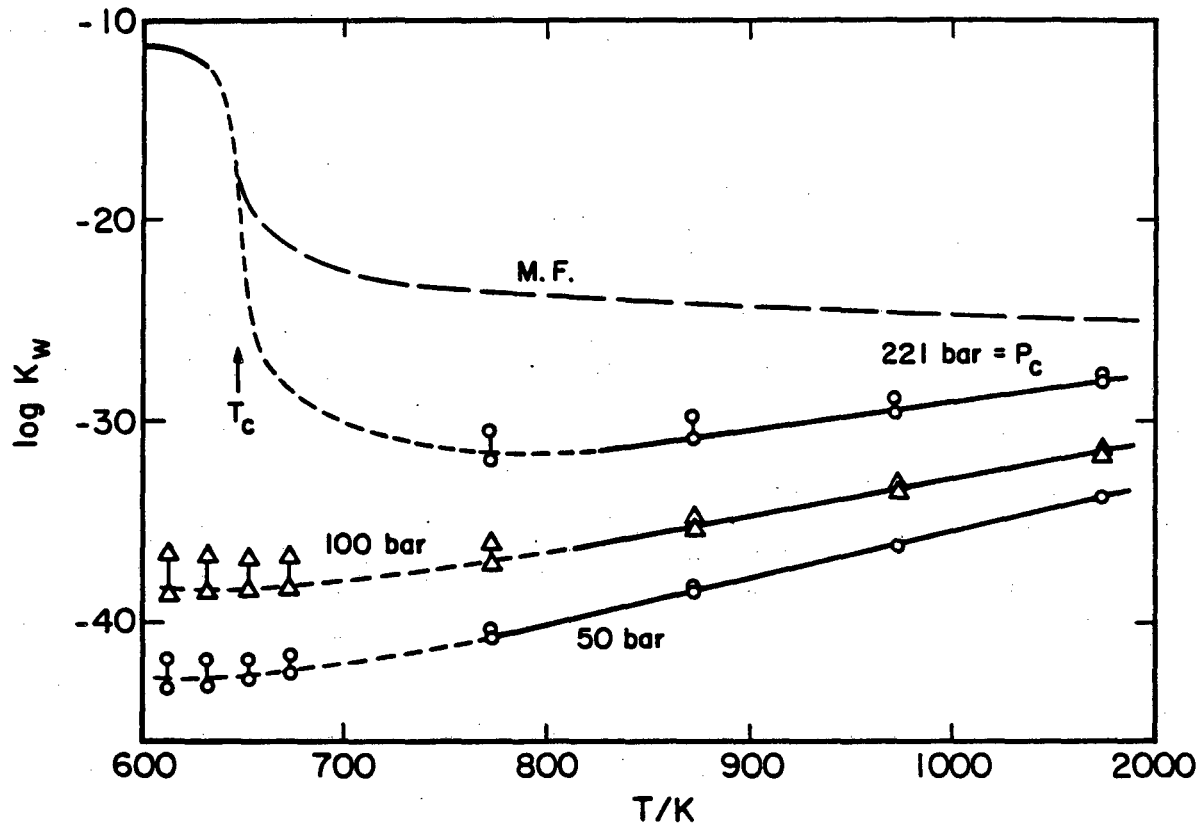


Figure 3. The ionization product in the critical region and at higher temperatures and several pressures; details are the same as for figure 1.

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