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Estimates of Thermodynamic Properties of H_2O in Equilibrium with H, H_2, O, O_2, and OH

Temperature 1000° to 6000° C and Pressure 10 to 250,000 Bars

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Pressure-volume-temperature measurements made at temperatures less than 1000° C. and pressures up to 250,000 bars are combined with chemical equilibrium calculations to give the thermodynamic properties of water from 1000° to 6000° C. and from 10 to 250,000 bars.

Pressure-volume-temperature measurements for water have been made at temperatures less than 1000° C. and pressures up to 250 kbars (*4, 9-12, 14*). These data have been used to determine thermodynamic properties in this pressure-temperature range (*8, 11, 16*). At higher pressures and temperatures, theoretical models have been used to estimate thermodynamic properties (*7, 13*). The present work combines chemical equilibrium calculations of dissociated water made by the present author with the data of Holser and Kennedy (*10*) and Rice and Walsh (*14*) to give thermodynamic functions for water in the temperature range 1000° to 6000° C. and pressures from 10 bars to 250 kbars. The chemical equilibrium calculations are similar to those Rybakov (*15*), but Rybakov does not list the reference conditions he assumed for his calculations and, consequently, his work cannot be compared with existing data. A reference energy state of the molecular species as ideal gases at 0° K. and 1 bar is used for the functions reported here. (0° K. is taken to be −273° C.)

The chemical equilibrium calculations were performed using the method due to Brinkley (*5, 6*), which is incorporated in the HUG computer code (*2*). Brinkley's method is based on a chemically reacting mixture of perfect gases in thermodynamic equilibrium. Dissociation products considered to be in the mixture are H, H_2, O, O_2, OH, and H_2O. The thermochemical data for these species were taken from the JANEF thermochemical tables, where they are tabulated up to 6000° K. (There is a slight extrapolation of these data, since the calculations were performed to 6000° C. = 6273° K.) Ionization was included in the calculations, but was found to be unimportant.

The perfect gas assumption is invalid if the specific volume is so small that intermolecular forces become important. Accordingly, the chemical equilibrium calculations were considered in error for specific volumes smaller than twice the critical volume, or about 6.4 cm^3 per gram. This criterion is based on comparison of experimental data with the perfect gas law.

METHOD

In general, a change in the Gibbs function is given by

$$dG = -SdT + VdP + \sum_i \frac{\partial G}{\partial n_i} dn_i$$

A change involving only equilibrium states at constant T and P requires

$$\sum_i \frac{\partial G}{\partial n_i} dn_i = 0$$

A closed system consisting of H_2O and its dissociation products in equilibrium is considered here. A change in this system involves only equilibrium states. Consequently,

$$dG = -S'dT + VdP$$

and G is a function of only T and P.
Thus

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P$$

and

$$\left(\frac{\partial V}{\partial T}\right) = \frac{\partial}{\partial T}\Big)_P \left(\frac{\partial G}{P}\right)_T = \frac{}{\partial P}\Big)_T \left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial S}{P}\right)_T$$

Tables relating temperature, pressure, and specific volume are constructed from the experimental data (*10, 14*) and the chemical equilibrium calculations. The values of $V(T, P)$ and $[\partial V(T, P)/\partial T]_P$ along isotherms are derived from these tables, interpolating where data are missing or incorrect. If the entropy, S, is known for some temperature T^* and pressure P^*, the entropy at the same temperature but another pressure is then found from

$$S(T^*, P) = S(T^*, P^*) - \int_{P^*}^{P} \left[\frac{\partial V(T^*, P')}{\partial T^*}\right]_{P'} dP' \qquad (1)$$

Similarly, the Gibbs free energy is found from

$$G(T^*, P) = G(T^*, P^*) + \int_{P^*}^{P} V(T^*, P')dP' \qquad (2)$$

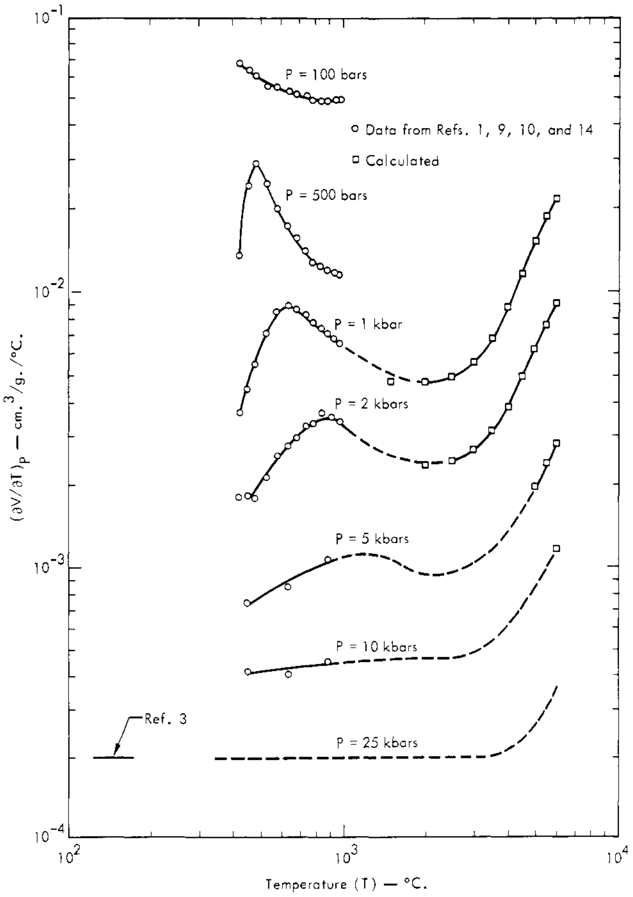

Figure 1. Pressure variation of $(\partial V/\partial T)_P$

The enthalpy is then

$$H(T, P) = G(T, P) + TS(T, P) \qquad (3)$$

Figure 1 shows curves of $(\partial V/\partial T)_P$, and data from Holser and Kennedy (*10*) and Rice and Walsh (*14*) [as reported by the American Institute of Physics (*1*)], points calculated from HUG, and a low-temperature measurement by Bridgman (*3*) at 25 kbars. The dashed portion of the curves is an interpolation. Figure 2 shows how the interpolation was made. In addition to the data used in Figure 1, there are some points calculated by HUG where the specific volume is less than twice the critical volume; consequently, these points are more uncertain. Following the assumption of Rice and Walsh (*14*), when the pressure is high enough, $(\partial V/\partial T)_P$ becomes independent of temperature and the curves come together on one line. All the calculated points lie on straight lines. The interpolation between HUG points and the data of Rice and Walsh is made by extending these straight lines, fairing them into the Rice and Walsh data in the manner indicated by the dashed lines. These straight-line extensions are replotted as dashed lines in Figure 1.

The specific volume is found by integrating $(\partial V/\partial T)_P$ along an isobar starting with the specific volumes at 1000° C. given by The American Institute of Physics (*1*) and Rice and Walsh (*14*)—that is,

$$V(T, P) = V(1000, P) + \int_{1000}^{T} \left[\frac{\partial V(T', P)}{\partial T'}\right]_P dT' \qquad (4)$$

The integration was performed using Simpson's rule. The results are shown in Figure 3.

Having determined $(\partial V/\partial T)_P$ and V, the entropy, Gibbs free energy, and enthalpy were calculated according to Equations 1 to 3. The integrals were evaluated, assuming $(\partial V/\partial T)$ and V could be approximated by a function of the form bP^a over an integration step ΔP, where b

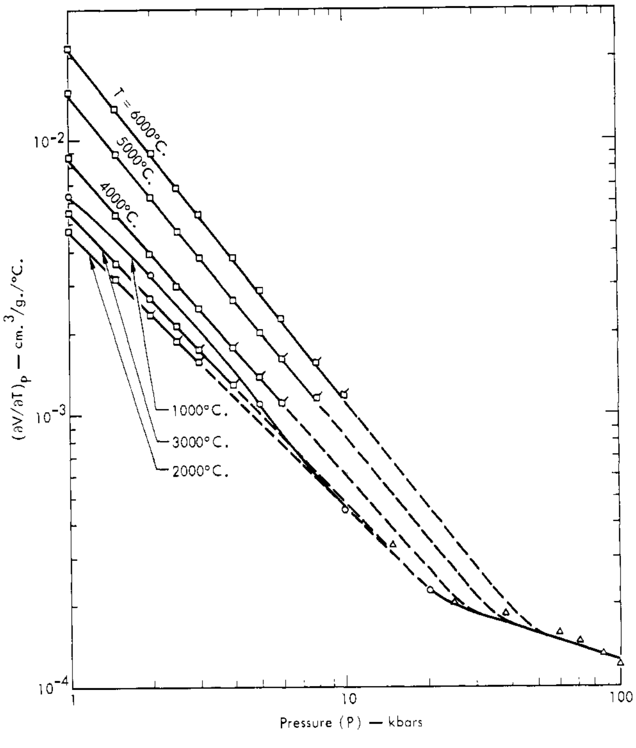

Figure 2. Temperature variation of $(\partial V/\partial T)_P$

□ HUG calculation
□́ HUG calculation $V/V_c < 2$
△ Rice and Walsh, Ref. 14
○ Ref. 1

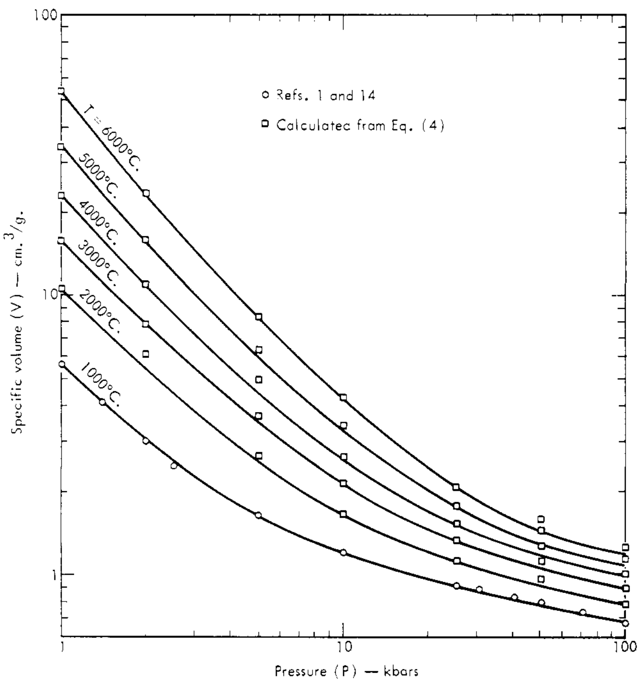

Figure 3. Specific volume

and a are constant throughout the step. Then

$$\int_{P_1}^{P_2}\left[\frac{\partial V(T,P')}{\partial T}\right]dP' \cong \int_{P_1}^{P_2} bP^a\,dP = \frac{1}{a+1}\left[P_2\left(\frac{\partial V}{\partial T}\right)_{P_2} - P_1\left(\frac{\partial V}{\partial T}\right)_{P_1}\right] \quad (5)$$

where

$$a = \frac{\ln\left[\left(\frac{\partial V}{\partial T}\right)_{P_2}\Big/\left(\frac{\partial V}{\partial T}\right)_{P_1}\right]}{\ln\,(P_2/P_1)} \quad (6)$$

and

$$P_2 = P_1 + \Delta P$$

Similarly,

$$\int_{P_1}^{P_2} V(T,P')\,dP' = \frac{1}{a'+1}\left[P_2\,V(T,P_2) - P_1\,V(T,P_1)\right] \quad (7)$$

and

$$a' = \frac{\ln[V(T,P_2)/V(T,P_1)]}{\ln(P_2/P_1)} \quad (8)$$

Table I. Specific Volume V(Cm.³/G.), Enthalpy H (Kcal./G.), Entropy S(Cal./G./° C.), and Gibbs Free Energy G(Kcal./G.) for Water

	P, Kbars									
	0.01	0.1	1	2	5	10	25	50	100	250
					T = 1000° C.					
V	587.3	58.38	5.717	3.18	1.616	1.22	0.9135	0.78	0.675	0.4835
H	0.63138	0.62384	0.55638	0.51681	0.50254	0.56339	0.80169	1.1674	1.8158	3.5057
S	2.9676	2.7094	2.4080	2.3000	2.1677	2.0859	1.9831	1.8778	1.7124	1.4645
G	−3.1464	−2.8257	−2.5090	−2.4110	−2.2570	−2.0920	−1.7229	−1.2231	−0.36400	1.6414
					T = 2000° C.					
V	1055	105.2	10.50	5.4	2.54	1.645	1.1135	0.93	0.776	0.5251
H	1.0737	1.0515	1.0408	1.0399	1.0624	1.1268	1.3642	1.7270	2.3585	4.0300
S	3.3670	3.1019	2.8429	2.7647	2.6626	2.5859	2.4823	2.3769	2.2115	1.9636
G	−6.5795	−5.9991	−5.4211	−5.2443	−4.9896	−4.7512	−4.2780	−3.6758	−2.6682	−0.43333
					T = 3000° C.					
V	1724	159.6	15.47	7.90	3.50	2.112	1.3135	1.07	0.894	0.5667
H	2.9910	2.0300	1.8150	1.7782	1.7652	1.8308	2.0592	2.4156	3.0258	4.6999
S	3.9513	3.4969	3.1643	3.0746	2.9605	2.8778	2.7712	2.6658	2.5004	2.2525
G	−9.9416	−9.4154	−8.5420	−8.2850	−7.9244	−7.5883	−7.0108	−6.3096	−5.1580	−2.6726
					T = 4000° C.					
V	2748	263.6	22.31	10.9	4.5	2.656	1.5162	1.19	1.012	0.6083
H	8.7372	5.0906	3.1713	2.9574	2.7588	2.7310	2.8842	3.2134	3.7949	5.4702
S	5.4511	4.1974	3.5643	3.4284	3.2694	3.1628	3.0381	2.9314	2.7660	2.5181
G	−14.555	−12.845	−12.059	−11.692	−11.211	−10.783	−10.097	−9.3125	−8.0241	−5.2897
					T = 5000° C.					
V	6670	484.2	33.90	15.78	6.1	3.381	1.7524	1.31	1.09	0.6499
H	14.823	10.138	5.4672	4.8200	4.2041	3.9749	3.9353	4.2201	4.7997	6.5609
S	6.7494	5.2524	4.1010	3.8759	3.6319	3.4809	3.3162	3.2026	3.0372	2.7893
G	−20.767	−17.558	−16.157	−15.617	−14.947	−14.397	−13.551	−12.667	−11.216	−8.1473
					T = 6000° C.					
V	8519	749.2	52.26	23.39	8.273	4.371	2.0621	1.46	1.20	0.6915
H	16.872	14.700	8.5475	7.3203	6.0889	5.5077	5.1148	5.2645	5.7951	7.4698
S	7.1108	6.0506	4.7107	4.3844	4.0343	3.8215	3.9563	3.4590	3.2936	3.0457
G	−27.734	−23.255	−21.003	−20.183	−19.219	−18.464	−17.445	−16.434	−14.866	−11.636

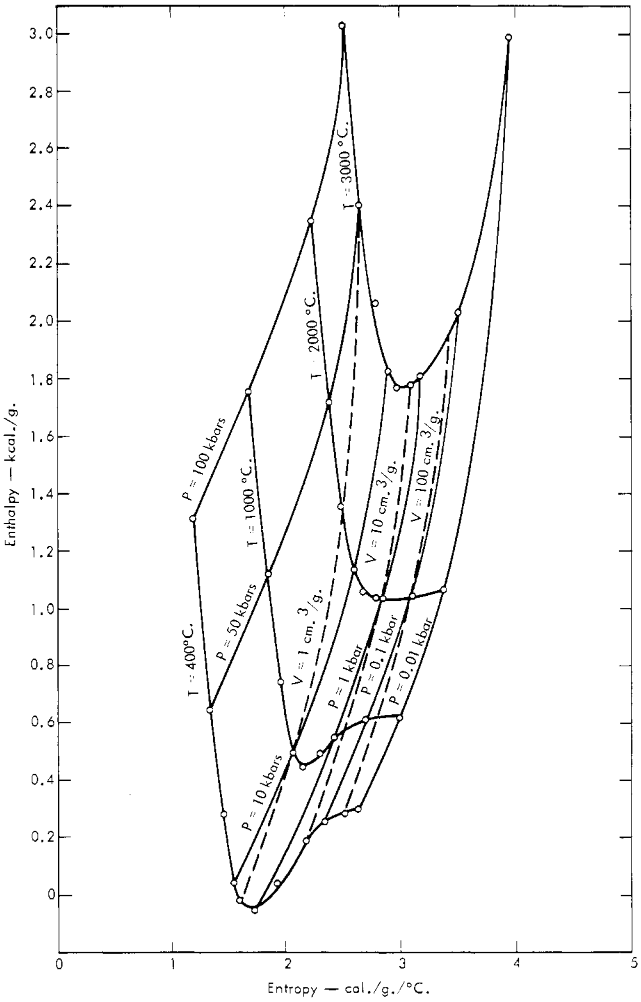

Figure 4. Mollier diagram, low temperatures

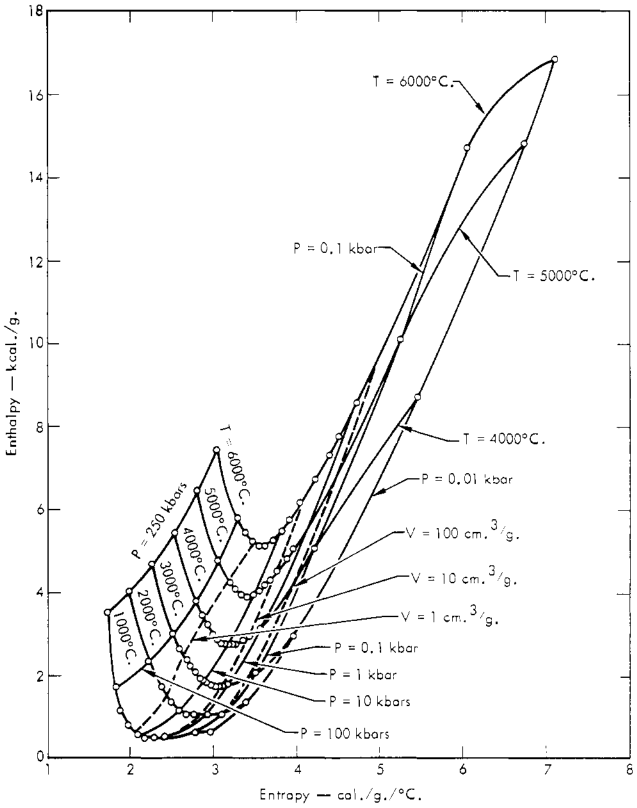

Figure 5. Mollier diagram, high temperatures

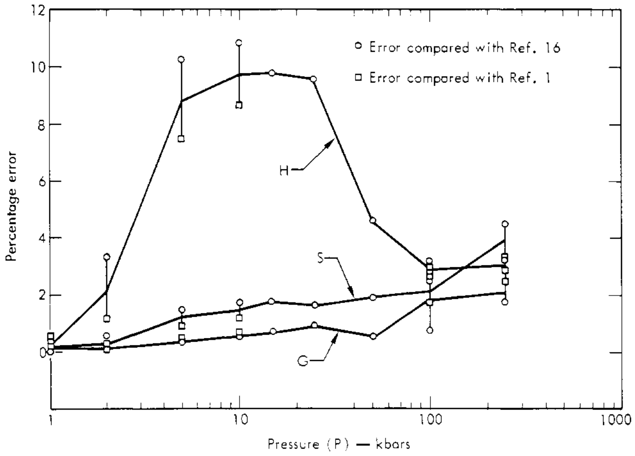

Figure 6. Error estimate

RESULTS

Results of the calculation are given in Table I and the enthalpy-entropy diagrams in Figures 4 and 5.

The calculational error can be estimated by comparing values obtained by the scheme outlined above along the 1000° C. isotherm with the values given (*1*, *14*). The error thus found is indicative of the error which will be made in using this scheme on the other isotherms. The percentage error on the 1000° C. isotherm is shown in Figure 6. As can be seen, the errors in entropy and Gibbs free energy appear to be acceptable. The error in enthalpy, however, becomes as great as ~10%, because the enthalpy depends on the difference between two numbers, *G* and *TS*, which are of comparable size.

The error also depends on the accuracy of the *P-V-T* data—that is, on the work of Holser and Kennedy (*10*) and Rice and Walsh (*14*). Holser and Kennedy did not measure *P-V-T* data at 1000° C., but obtained them by extrapolation of measurements at lower temperatures and pressures. In addition, the isotherms given by Rice and Walsh are derived from data on the Hugoniot curve, by making certain assumptions about the specific heat at constant pressure and $(\partial V/\partial T)_P$. Consequently, the thermodynamic properties derived here are not precise, but they are a reasonable estimate.

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Solubility of F_2, NF_3, and O_2 in Anhydrous Liquid HF

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The solubility of F_2, NF_3, and O_2 in anhydrous liquid HF was measured at several temperatures. The solubility of F_2 passes through a minimum between −0.21° and 19.8° C., but between −0.21° and −77.2° C. it can be computed to within 3% of the observed value. The heat of solution is −588 cal. $mole^{-1}$. The solubility of NF_3 was measured at three temperatures; it does not exhibit a solubility minumum similar to that of F_2. At −77.2° C. a curved plot of partial pressure *vs.* molality was observed at pressures exceeding 1 atm. The heat of solution is −1533 cal. $mole^{-1}$. The solubility of O_2, measured at −0.21° and 19.8° C., was similar to that of F_2. A heat of solution calculated from the solubility at these two temperatures is −352 cal. $mole^{-1}$. The solubility of O_2 in HF at 19.8° and −0.21° C. was larger by factors of 5 and 10, respectively, than the literature values for solubility in H_2O at the same temperatures.

The solubility of gases in liquids is of theoretical interest, and when measured with sufficient precision and sensitivity can be used along with other information such as conductivity to infer the presence or absence of interaction of the gas with the solvent. In our study of the chemistry of NF_3 and F_2 in liquid HF, it was of interest to determine their solubilities in this solvent. The solubility of O_2 in HF was also determined. These data permit comparison of the solubility of O_2 in HF and in H_2O. A similar comparison of the solubility of F_2 in the two solvents would have little value, because F_2 reacts with water.

EXPERIMENTAL

The method was similar to that of Kilpatrick and Luborsky (*2*), who with others (*1, 3*) have reported the solubility of BF_3 in liquid HF. In the present work, solubility measurements were made at several temperatures in a constant temperature bath. A Kontes K-87250 Model A thermoregulator provided room temperature regulation to ±0.2° C. The thermometer used for room temperature readings was calibrated against a platinum resistance thermometer. Slush baths were used to obtain temperatures lower than ambient. The temperature of the slush bath was determined with a $CFCl_3$ gas thermometer connected to a calibrated Wallace and Tiernan gage. A comparison of the pressure within the gas thermometer to that of the known vapor pressure curve for $CFCl_3$ gave the temperature of the slush bath. Thus, temperatures lower than ambient given in this paper are only as accurate as the Wallace and Tiernan gage and the known vapor pressure curve for $CFCl_3$.

The apparatus shown in Figure 1 was fabricated from Monel metal and assembled by brazing with silver solder.

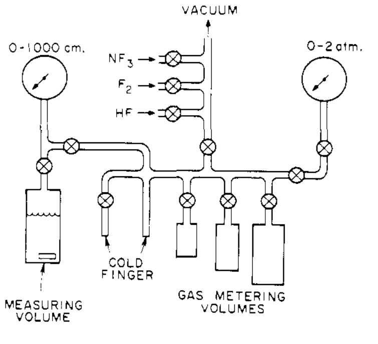

Figure 1. Solubility apparatus