sulfide, 14.5% carbon dioxide respectively (Figure 5 or 7).

Isothermal compression of the 60% hydrogen sulfide mixture from the vapor phase at −133°F. shows that at 4.4 lb./sq. in. abs. the vapor is in equilibrium with incipient solid hydrogen sulfide and liquid. Continued compression causes the system to enter the vapor-liquid region until at 6.5 lb./sq. in. abs. solid carbon dioxide forms. At the latter condition vapor and liquid in equilibrium with solid carbon dioxide have compositions of 32.5% hydrogen sulfide, 67.5% carbon dioxide and 86% hydrogen sulfide, 14% carbon dioxide respectively.

If compression from the vapor phase for the 60% hydrogen sulfide mixture now occurs at −137°F., solid hydrogen sulfide forms. Upon further compression liquid forms at a vapor-liquid-solid hydrogen sulfide triple point at −137°F. and 4.7 lb./sq. in. abs. Vapor and liquid compositions at this point are 45% hydrogen sulfide, 55% carbon dioxide and 91% hydrogen sulfide, 9% carbon dioxide respectively. Vapor and liquid exist at pressures between 4.7 and 5.5 lb./sq. in. abs. at −137°F. At 5.5 lb./sq. in. abs. and −137°F. vapor, liquid, and solid carbon dioxide coexist where vapor composition is 33% hydrogen sulfide and liquid composition is 87% hydrogen sulfide.

Similar analyses can describe the behavior of any mixture in the low-temperature region. As directly indicated on Figures 5 to 7 systems containing between 12.5 and 66 mole % carbon dioxide have triple points at which vapor, liquid, and either solid hydrogen sulfide or solid carbon dioxide are in mutual equilibrium. Those mixtures with more than 66 mole % carbon dioxide can have vapor and liquid in equilibrium only with solid carbon dioxide; those with less than 12.5 mole % carbon dioxide have triple-point equilibria with solid hydrogen sulfide.

In view of the availability of the phase data at temperatures down to the solid-liquid-vapor loci of the three binary systems which comprise the methane-hydrogen sulfide–carbon dioxide ternary system, it is interesting to speculate about the behavior of the ternary.

It would be particularly interesting to know what influence carbon dioxide has upon the heterogeneous liquid-liquid-vapor behavior reported for the methane-hydrogen sulfide system (*5*).

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The Enthalpy of Water in the Liquid State

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The enthalpy of water in the liquid state has been calculated from 32°F. to temperatures approaching the critical and pressures ranging from saturated conditions to 160,000 lb./sq. in. abs. (approximately 11,000 atm). The results of this study are presented graphically and show that the influence of pressure on enthalpy is significant, particularly in the lower temperature region. At these conditions pressure is found to increase the enthalpy of liquid water by as much as 360 B.t.u./lb. above the corresponding enthalpy of the saturated liquid state.

A comprehensive literature search disclosed PVT data for water that permitted the construction of a density correlation. This correlation expressed in reduced coordinates extends from the normal freezing point of water to temperatures of 1,870°F. ($T_R = 2.0$) and pressures ranging up to 10,915 atm. ($P_R = 50$). The recent extensive PVT data of Kennedy reported in 1950 supplemented with the earlier data of Amagat and Bridgman allowed the calculation of enthalpies at these elevated temperatures and pressures. For these calculations basic thermodynamic relationships were adapted which utilized this reduced density correlation. This approach has made possible the extension of the thermodynamic properties of liquid water above the highest pressure reported by Keenan and Keys. Below this pressure of 6,000 lb./sq. in abs. good agreement was found to exist between the enthalpy values presented by Keenan and Keyes and those reported in this investigation.

Considerable information is presented in the literature on the thermodynamic properties of nonpolar compounds. These substances are composed of electrically symmetrical molecules which tend to behave as perfect gases or ideal solutions. The hydrocarbons are characteristic of this class of compounds for which thermodynamic properties can be readily predicted from generalized thermodynamic correlations. The prediction of these thermodynamic properties for nonpolar substances depends upon the critical temperature and pressure and, as recently proposed by Meissner and Seferian (*24*), also upon the critical compressibility factor.

For nonpolar substances such as argon, nitrogen, and methane the critical compressibility factors extend up to a value of 0.291. Values of the critical compressibility factors for helium, hydrogen, and neon are yet higher ($z_c = 0.307$); however these substances fail to follow the theorem of corresponding states, as expected from their identical critical compressibility factors. This abnormal behavior is attributed to quantum effects which are significant for these three substances. Conversely polar substances have characteristically lower z_c values; for example, water and methyl alcohol have z_c values of 0.231 and 0.222, respectively. The lowest z_c value is reported by Lydersen, Greenkorn, and Hougen (*23*) as 0.197 for hydrogen cyanide. Other substances reported in the literature have critical compressibility factors ranging from 0.231 to 0.291.

The direct association of polarity and the critical compressibility factor of substances is apparent, thus leading to the qualitative generalization that substances having high dipole moments are always associated with low critical compressibility factors. Since water is characteristic of substances having high dipole moments ($\mu = 1.87$ debye units) (*38*), its thermodynamic properties cannot be accurately developed from existing generalized correlations (*9, 12*). Therefore water has been selected as typical of those compounds which must be treated individually for an evaluation of their thermodynamic properties. This investigation is concerned with the calculation of enthalpy for water in the liquid state at elevated temperatures and pressures. The results of this study permit the extension of the enthalpies reported by Keenan and Keyes (*16*) from pressures of 6,000 to 160,000 lb./sq. in. abs. and temperatures up to 650°F.

REDUCED-STATE DENSITY CORRELATION

A comprehensive literature search for density data of water has resulted in a compilation showing the dependence of density on both temperature and pressure. Experimental densities for the liquid and gaseous states including values in the critical region have been considered in this study. The critical constants for water reported by Kobe and Lynn (*22*) were used to calculate reduced temperatures, pressures, and densities. These critical constants are $T_c = 647.4$°K., $P_c = 218.3$ atm., and $\rho_c = 0.32$ g./cc.

Since the majority of density data could not be conveniently expressed as a function of reduced pressure, it became necessary to cross-plot the original density data in order to obtain reduced densities at the appropriate reduced pressures. Figure 1 presents the final correlation of reduced density for water. In this compilation the saturated density data of Batelli (*2, 3*), Mendelejeff (*25*), Perot (*29*), Waterston (*37*), and Wüllner and Grotrian (*39*) obtained before the turn of the century were found to be in good agreement with the data of a number of invesitgators (*8, 10, 15, 18, 35*) who later reported density data for the saturated envelope. The experimental high-pressure data of Amagat (*1*) and Bridgman (*5, 6*) for liquid water cover the temperature range of −20° to 198°C. and account for densities up to pressures of 160,000 lb./sq. in. abs. Of particular interest are the data reported in 1950 by Kennedy (*17*) which permit the extension of the reduced density correlation into temperature and pressure regions where no data were previously available. Consequently densities now can be defined in the temperature region of $0.6 \leq T_R \leq 1.35$ to pressures as high as $P_R = 10$ (2,183 atm.) and for the higher temperature region of $1.35 \leq T_R \leq 2.00$ up to pressures of $P_R = 6.0$ (1,310 atm.).

In Figure 1 the density correlation has been presented on rectilinear coordinates to accentuate the regions of interest for water in the liquid state. Reduced-state correlations of this type, as well as those expressed on logarithmic coordinates, are receiving considerable attention in attempts to generalize the PVT behavior of substances. In addition to the correlating parameters of reduced temperature and pressure, Lydersen, Greenkorn, and Hougen (*23*) have utilized the critical compressibility factor as the third correlating parameter in their studies involving the thermodynamic properties of substances.

THERMODYNAMIC TREATMENT

The enthalpy change of a system as a function of temperature and pressure can be expressed in differential form as

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (1)$$

Equation (1) is equivalent to the thermodynamic relationship

$$dH = C_p\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \qquad (2)$$

where

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p$$

and

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

TABLE 1. ENTHALPY DIFFERENCES FOR COMPRESSED LIQUID WATER (LOW-PRESSURE REGION)

Pressure, lb./sq. in. abs.	$h - h_s$, Enthalpy difference, B.t.u./lb. 32°F.	50°F.	100°F.	150°F.	200°F.	250°F.	300°F.	350°F.	400°F.	450°F.	500°F.	550°F.	600°F.	650°F.
1,000	2.9	2.8	2.6	2.4	2.1	2.0	1.9	1.3	1.0	0.3	−0.1			
2,000	5.5	5.3	5.1	4.8	4.5	4.0	3.6	2.9	2.0	0.9	−0.6	−1.6	−1.8	
3,000	8.1	8.0	7.7	7.1	6.8	6.1	5.6	4.4	3.2	1.5	−0.6	−2.9	−5.3	−7.4
4,000	10.9	10.8	10.1	9.7	9.0	8.2	7.5	6.0	4.4	2.1	−0.3	−3.9	−8.3	−14.6
5,000	13.6	13.5	12.9	12.1	11.3	10.3	9.3	7.7	5.7	3.0	−0.1	−4.7	−10.7	−20.1
6,000	16.2	16.1	15.4	14.7	13.7	12.7	11.2	9.3	7.0	4.1	0.2	−5.2	−12.2	−24.2
8,000	21.8	21.6	20.6	19.6	18.3	17.0	15.2	12.9	9.9	6.2	1.3	−5.3	−14.5	−30.1
10,000	27.1	26.9	25.7	24.4	22.9	21.2	19.1	16.5	13.0	8.9	3.1	−5.6	−15.2	−33.7
12,500	34.0	33.6	32.1	30.5	28.7	26.6	24.1	21.1	17.1	12.2	5.8	−2.9	−15.2	−35.6
15,000	40.6	40.1	38.3	36.6	34.4	32.1	29.1	26.0	21.4	16.1	8.9	−0.6	−14.3	−35.8
17,500	47.1	46.7	44.7	42.7	40.2	37.5	34.2	30.9	25.9	19.9	12.2	2.0	−12.7	−35.3
20,000	53.7	53.0	51.0	48.9	46.2	43.1	39.4	35.7	30.3	24.0	16.0	4.9	−10.2	−34.1
25,000	66.4	65.7	63.1	60.7	57.6	54.0	49.9	45.6	39.6	32.9	23.6	11.2	−4.9	−30.5
30,000	78.9	77.9	75.1	72.3	69.0	65.1	60.7	55.6	49.0	41.9	31.7	18.2	1.2	−25.2
35,000	90.9	89.9	87.1	84.0	80.2	76.2	71.7	65.7	58.8	50.5	39.9	25.9	7.9	−18.5

Reference state: h_s = enthalpy of water at saturated-state conditions

In order to utilize the density information presented in Figure 1, the following substitutions for pressure, temperature, and density were used:

$$P = P_c P_R, \qquad T = T_c T_R$$

and

$$V = \frac{M}{\rho_c \rho_R}$$

to produce Equation (3), which relates the effect of pressure on enthalpy above a reference state that has been selected as the enthalpy of liquid water at its corresponding vapor pressure:

$$\int_{h_s}^{h} dH = \frac{MP_c}{\rho_c} \cdot \int_{(P_R)_{v.p}}^{P_R} \left[\frac{1}{\rho_R} + \frac{T_R}{\rho_R^{2}} \left(\frac{\partial \rho_R}{\partial T_R} \right)_{P_R} \right] dP_R \qquad (3)$$

Equation (3) permits the calculation of enthalpy changes due to pressure at isothermal conditions. Integration of Equation (3) requires the evaluation of the function

$$f(\rho_R, T_R) = (1/\rho_R) + (T_R/\rho_R^2)(\partial \rho_R/\partial T_R)_{P_R}.$$

Graphical differentiation utilizing the chord-area method has been employed to produce the slopes $(\partial \rho_R/\partial T_R)_{P_R}$ from Figure 1 as functions of reduced temperature for constant parameters of reduced pressure. The pressures considered ranged from the saturated state to $P_R = 50$ in the temperature interval $0.422 \leq T_R \leq 0.6$ and to $P_R = 10$ in the temperature interval $0.6 \leq T_R \leq 1.20$. Utilizing this information, one could directly obtain the dimensionless quantity

$$(1/\rho_R) + (T_R/\rho_R^2)(\partial \rho_R/\partial T_R)_{P_R}$$

for the temperature interval $0.422 \leq T_R \leq 0.95$. The function $f(\rho_R, T_R)$ did not become negative until the reduced temperature became $T_R = 0.85$. These negative values can be explained from the fact that the negative contribution of the quantity $(T_R/\rho_R^2)(\partial \rho_R/\partial T_R)_{P_R}$ becomes larger than the quantity $(1/\rho_R)$ for $T_R \geq 0.85$. With this information Equation (3) was graphically integrated for a number of constant temperatures between the limits of the reduced vapor pressure and reduced pressure. The results of this procedure produced enthalpy changes due to pressure above the reference saturation pressure. For these calculations the vapor pressures compiled by Keenan and Keyes (*16*) have been used.

The results of this study are presented in Table 1 and also graphically in Figure 2 for pressures up to 35,000 lb./sq. in. abs. and for temperatures up to 650°F. Keenan and Keyes (*16*) present enthalpy differences for liquid water at pressures up to 6,000 lb./sq. in. abs. Values reported by Keenan and Keyes and those resulting from this study are found to be in agreement. Enthalpy differences for pressures above 35,000 lb./sq. in. abs. are presented in Table 2 for temperatures ranging from 32° to 250°F. and for pressures as high as 160,000 lb./sq. in. abs.

ENTHALPY OF SATURATED LIQUID WATER

The majority of heat-capacity data available are restricted to low temperatures. Rossini (*28*) points out that at present the data of Osborne, Stimson, and Ginnings (*27*) are the most reliable for the heat capacity of water up to

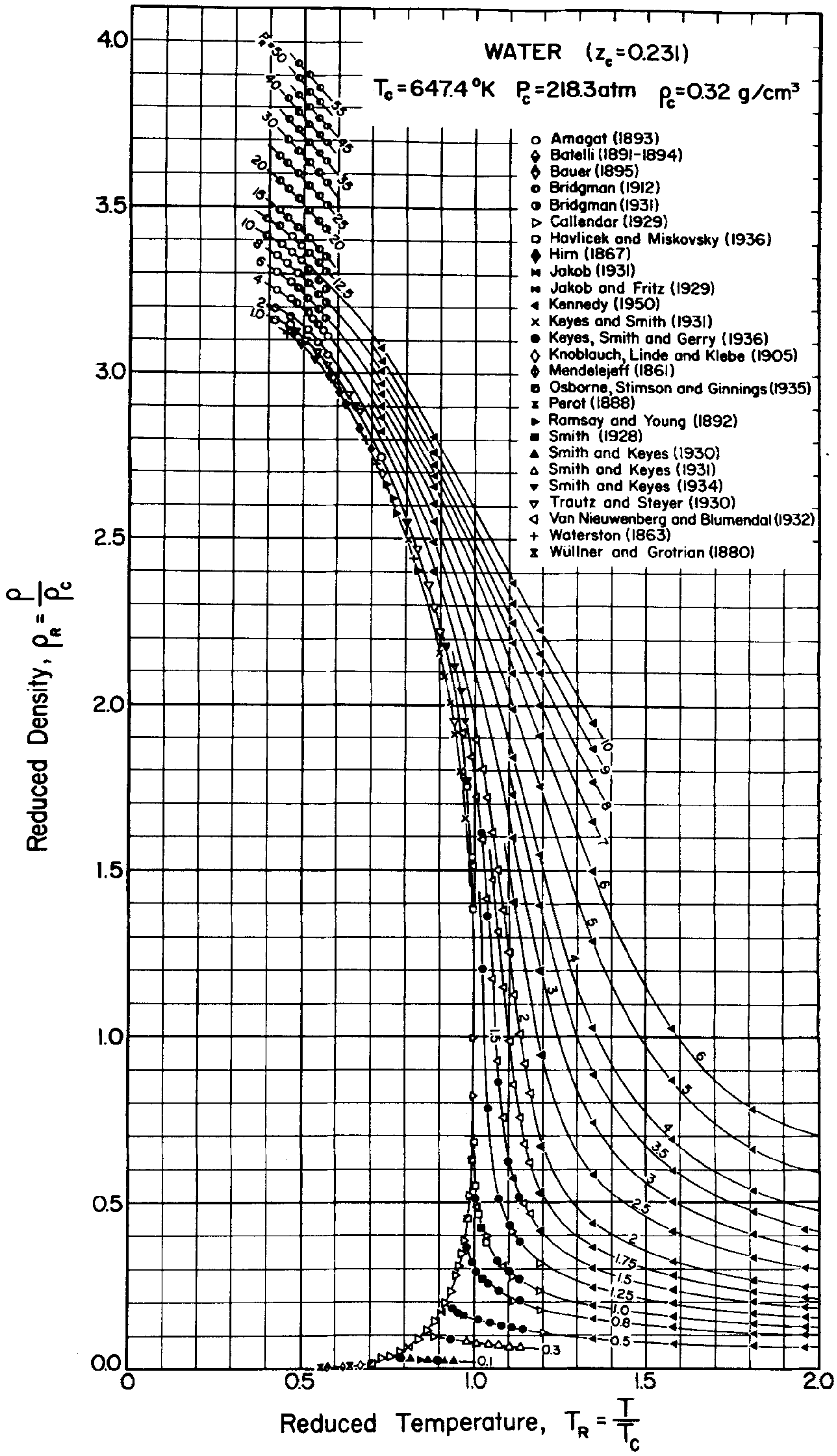

Fig. 1. Reduced-density correlation for water (rectilinear coordinates).

212°F. Since temperatures up to 650°F. have been considered in this study, their data were of restricted value. Because of the temperature limitation of their data, the constant-pressure heat-capacity data of Koch (*20*) were utilized to establish the enthalpy of water in the saturated liquid state up to 650°F.

For this analysis the heat-capacity data of Koch at 150 and 300 atm. were graphically integrated to produce the respective enthalpies above a reference state of 32°F. Enthalpy changes, $h - h_s$, for pressure effects, as obtained from Figure 2, made possible the calculation of enthalpies for the corresponding saturated liquid state. The following representative values are summarized:

		Koch (*20*)	
°F.	Keenan and Keyes (*16*)	150 atm.	300 atm.
200	168.0	167.6	167.2
400	375.0	374.7	373.5
600	617.0	615.3	613.8

The results produced from Koch's data at 150 atm. are in closer agreement with the values reported by Keenan and Keyes (*16*). This comparison appears acceptable, particularly since the saturated enthalpy values for the liquid state have been obtained by an approach different from that employed by Keenan and Keyes (*16*). The calculation of enthalpies for the saturated liquid state with the data of Koch used has been carried out in order to establish these values directly from data for the liquid state. The agreement of these values and those reported by Keenan and Keyes appears reasonable. Therefore the values reported by Keenan and Keyes have been accepted to produce the saturated enthalpy values presented in Figure 3.

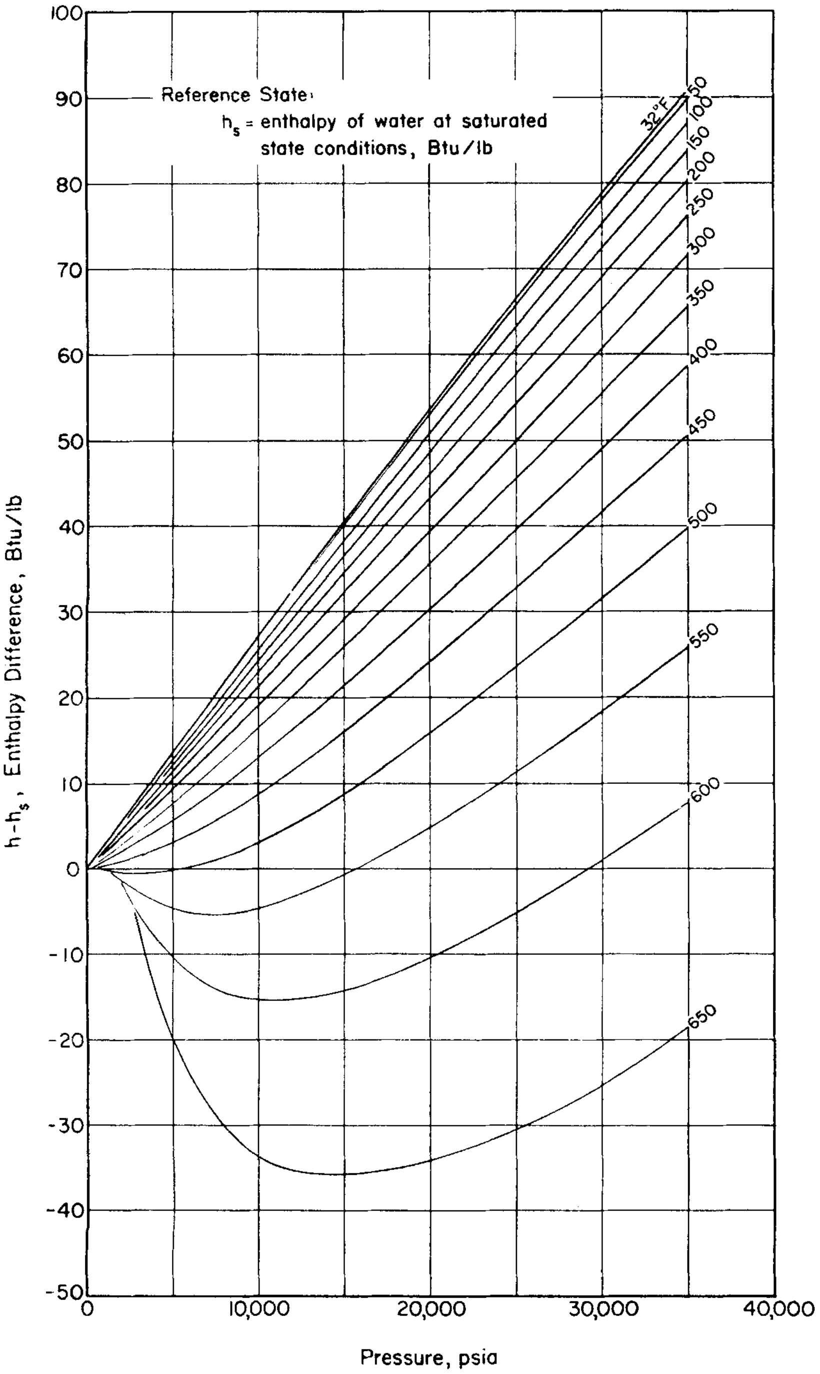

Fig. 2. Effect of pressure on enthalpy of liquid water.

The enthalpy differences for compressed liquid water presented in Tables 1 and 2 have been consolidated with the saturated enthalpy of liquid water to produce Figure 3. The isobars of 10,000, 20,000, and 30,000 lb./sq. in. abs. extend to 650°F., while those of higher pressures were limited to temperatures of 250°F. Restrictions have been imposed on the low-temperature range to account for the polymorphic behavior of water (*13*) in the formation of the different types of ices.

NOTATION

C_p = molar heat capacity at constant pressure, cal./(g.-mole) (°K.)
h = enthalpy for liquid state, B.t.u./lb.
h_s = enthalpy for saturated liquid state, B.t.u./lb.
H = enthalpy
M = molecular weight, g./g.-mole
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
$(P_R)_{v.p.}$ = reduced vapor pressure
R = gas constant
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
V = volume, cc./g.-mole
V_c = critical volume, cc./g.-mole
z_c = critical compressibility factor, P_cV_c/RT_c
μ = dipole moment, debye units
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c

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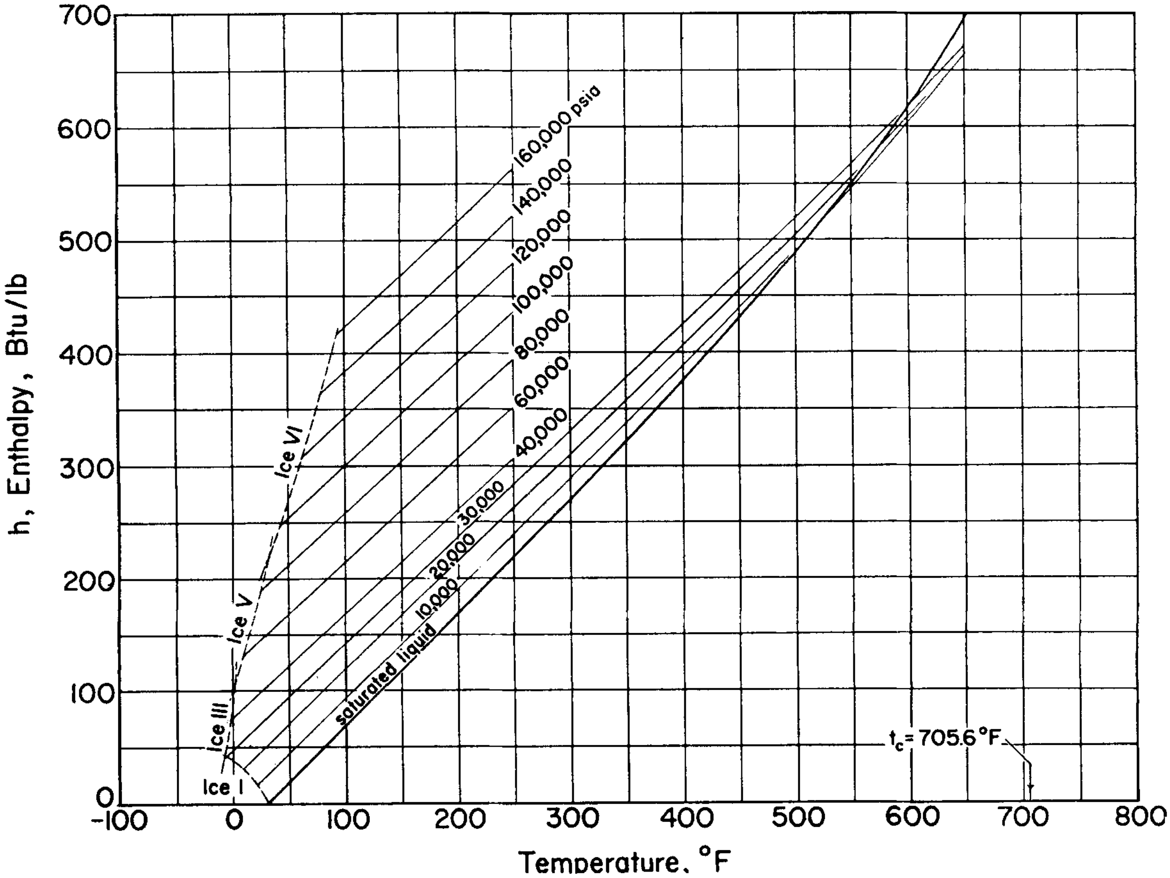

Fig. 3. Enthalpy of liquid water.

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TABLE 2. ENTHALPY DIFFERENCES FOR COMPRESSED LIQUID WATER (HIGH-PRESSURE REGION)

$h - h_s$, Enthalpy difference, B.t.u./lb.

t, °F.	40,000 lb./sq. in. abs.	60,000 lb./sq. in. abs.	80,000 lb./sq. in. abs.	100,000 lb./sq. in. abs.	120,000 lb./sq. in. abs.	140,000 lb./sq. in. abs.	160,000 lb./sq. in. abs.
32	102.7	149.9	194.6	238.0	279.9	320.8	360.2
50	101.8	148.8	193.3	236.6	278.3	319.2	359.2
100	99.0	145.5	189.6	232.1	274.0	314.9	355.8
150	95.9	141.7	185.2	227.2	269.3	310.3	352.0
200	92.1	136.6	179.9	222.3	264.5	305.9	347.6
250	87.8	131.2	174.1	216.7	259.1	301.1	342.8

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