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Washington, D.C. American Meteorological Society

P.J. Kiefer, "The thermodynamic properties of water and water vapor," Monthly Weather Review, v. 69, no.11, (November 1941), pp. 329-332.
<http://hdl.handle.net/10945/55923>

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MONTHLY WEATHER REVIEW

Editor, EDGAR W. WOOLARD

VOL. 69, No. 11
W. B. No. 1341

NOVEMBER 1941

CLOSED JAN. 3, 1942
ISSUED JAN. 27, 1942

THE THERMODYNAMIC PROPERTIES OF WATER AND WATER VAPOR

By PAUL J. KIEFER

[U. S. N. Postgraduate School, Annapolis, Md., June 1941]

Extensive international research has been conducted within about the last 10 years for the purpose of ascertaining, with maximum accuracy, the thermodynamic properties of water and water vapor. Experiments were carried out to this end at the National Bureau of Standards, the Massachusetts Institute of Technology, and Harvard University in the United States; and other experiments were conducted by agencies in England, Germany, and Czechoslovakia. By international conferences, the individual findings of these agencies were then collected and cross-checked for consistency by means of the general thermodynamic equations; when inconsistencies were disclosed, the apparatus was investigated and the data redetermined. The final results have been made available in this country in tables of the *Thermodynamic Properties of Steam*, prepared by J. H. Keenan and F. G. Keyes of the Massachusetts Institute of Technology (New York, John Wiley and Sons, 1936).

The range of pressures and temperatures covered by these data extends far beyond that which is of importance to the meteorologist, as the project was sponsored by the American Society of Mechanical Engineers and hence included the properties at the high pressures and temperatures employed in power generation. However, both the extreme care taken and the wide range covered would seem to make the results exceptionally reliable within the lesser range that is of meteorological concern.

From these tables, the writer has therefore prepared the accompanying tabulation of some of the properties of water in the solid, liquid, and vapor states, over the range from -40°C. to $+50^{\circ}\text{C.}$ In preparing this tabulation, the units of temperature, pressure, and energy were changed from those conventionally employed by the engineer in this country to the ones preferred by the meteorologist; and various thermodynamic checks were employed to insure consistency in the results.

The first three columns of the table contain the temperatures and the corresponding saturated vapor pressures and densities; the latter are given both for ordinary equilibrium conditions throughout the temperature range of the table, and also for vapor in equilibrium with subcooled water.

Over the range of the table, the saturated vapor pressures of the liquid phase may be represented with great accuracy by the equation

$$\ln(p/p_0) = 6887(1/T_0 - 1/T) - 5.31 \ln(T/T_0); \quad (1)$$

or, taking T_0 as the ice-point temperature 273°K. (or

more exactly, $273^{\circ}.16$) and p_0 as the corresponding saturation pressure of 6.105 mb., we have

$$\ln\left(\frac{p}{6.105}\right) = 25.21 \frac{t}{t+273} - 5.31 \ln \frac{t+273}{273}, \quad (1a)$$

$$\text{or} \quad \log_{10}\left(\frac{p}{6.105}\right) = 10.95 \frac{t}{t+273} - 5.31 \log_{10} \frac{t+273}{273}. \quad (1b)$$

Equation (1) conforms to the requirements of the Clapeyron equation (see Brunt, *Physical and Dynamical Meteorology*, 2 ed., pp. 101-104). The form (1b) may be compared with the relation

$$\log_{10}\left(\frac{p}{6.105}\right) = 10.78 \frac{t}{t+273} - 5.01 \log_{10} \frac{t+273}{273}$$

proposed by Whipple (MONTHLY WEATHER REVIEW, 55: 131, 1927).

For the range of ice-vapor states, Keenan and Keyes accepted the data given by Washburn, MONTHLY WEATHER REVIEW 52:488-490, 1924, although they noted that some thermodynamic inconsistency exists in these data. Slight inconsistencies in this range, however, are of minor concern to the meteorologist because of the very small mixing ratios that are associated with it. The Washburn pressure-temperature data may be represented by the relation

$$\ln(p/p_0) = 4332(1/T_0 - 1/T) + 2.31 \ln(T/T_0).$$

It may be shown that the requirements of the Clapeyron equation would be more nearly met by a relation of the form

$$\ln(p/p_0) = 6150(1/T_0 - 1/T),$$

or one approaching the Whipple relation for the ice-vapor states,

$$\ln(p/p_0) = 6260(1/T_0 - 1/T) - 0.445 \ln(T/T_0).$$

The density, pressure, and temperature data in the table show the ratio $p/\rho T$ to be substantially constant, with the value 0.461 joules/(gm., $^{\circ}\text{K.}$). This fact justifies the commonly accepted hypothesis that water vapor, at the low pressures that are of concern to the meteorologist, may be regarded as a perfect gas; and also confirms the values of the perfect gas constant that have been regularly employed for water vapor in meteorological literature.

The quantities in the next three columns of the table, viz, h_f , h_{fg} , h_g , and h_t , h_{tg} , h_g , are in a sense those that have long been referred to in the literature as, respectively, the "total heat of the liquid (or the solid)," the "latent heat

of vaporization (or sublimation)" and the "total heat of the vapor." It may seem that the use of the above symbols and the technical name "enthalpy" is a matter merely of change of nomenclature; it is, however, somewhat more than that, and the use of a distinctive term such as enthalpy (*en-thäl'-py*) to designate these functions has become virtually universal in the engineering and chemical professions within the last decade.

One reason for the adoption of this practice is that much unnecessary confusion has resulted from the indiscriminate use of the same word *heat* to designate several essentially different quantities, as, e. g.: (a) energy which is transferred by radiation or conduction between a system and its environment, producing changes of state in each, but not itself a function of the state of either; (b) internal energy, stored in a system by reason of its molecular and atomic state, and depending on the thermodynamic state of the system; (c) this stored energy plus the product of the pressure and specific volume, this sum frequently being known as the "total heat"; (d) even the temperature, although technical literature cannot be generally accused of this usage.

To avoid confusion, it has now become the accepted practice in engineering literature to employ the word *heat* (symbol, Q) only for the energy that may enter or leave a system by thermal radiation or conduction, just as the word *work* relates only to energy entering or leaving by mechanical processes; this meaning is the one implied in connection with "specific heats" or "adiabatic" processes. Heat, so understood, may not be regarded as a function of the state of a substance.

The energy that is stored in the molecular system of a substance is designated as its molecular or internal energy (symbol, E). Although we have no means for an absolute evaluation of the energy so stored, its relative amount per unit mass is determinable, and is a function of the state of the substance.

The further function of state given by the sum of the internal energy E and the product of the pressure P by the specific volume V is the one referred to above as the enthalpy: $H = E + PV$.

The general significance of this function may be illustrated by the so-called "steady-flow energy equation," $gZ_1 + U_1^2/2 + E_1 + P_1V_1 + {}_1Q_2 = gZ_2 + U_2^2/2 + E_2 + P_2V_2$, (2) a formulation of the principle of the conservation of energy (First Law of Thermodynamics) as applied to a stream of fluid flowing steadily into and out of any selected region. E.g., in a steadily ascending convective current in the atmosphere, subscripts (1) and (2) refer to a lower elevation Z_1 and an upper elevation Z_2 . The quantities gZ_1 and gZ_2 are then the potential energy or geopotential per unit mass at those levels; $U_1^2/2$ and $U_2^2/2$ are the kinetic energies per unit mass (U =velocity); E_1 and E_2 , the initial and final internal energy per unit mass; and ${}_1Q_2$ represents the heat energy absorbed or emitted per unit mass between the two levels, vanishing if the process be effectively adiabatic.

The products P_1V_1 and P_2V_2 represent the mechanical energy expended in the work done by the action of the force in effecting the flow of each unit mass against the pressures existing at the two levels: To sustain a flow over a cross section A into a region at pressure P , requires a force PA ; the distance L through which that force must act to effect the entry of a unit mass of fluid of volume V equals V/A ; and the "flow-work" energy so entering the region is thus $PA \frac{V}{A} = PV$.

Now in equation (2), E , P and V are each functions of the state, so that the quantity $(E + PV)$ must likewise be a function of state; and since the latter quantity must invariably appear in the energy equation for any flow process, it is advantageous to identify it by a single name and symbol—the enthalpy, H . Then equation (2) for steady flow becomes

$$gZ_1 + U_1^2/2 + H_1 + {}_1Q_2 = gZ_2 + U_2^2/2 + H_2, \quad (3)$$

or in differential form,

$$gdZ + UdU + dH = d'Q. \quad (3a)$$

For flow with negligible change of elevation and velocity, $dH = d'Q$ or ${}_1Q_2 = H_2 - H_1$; i. e., since such flow can occur only at constant pressure, the change of the enthalpy function for a fluid during an isobaric process evaluates the energy concurrently entering or departing by radiation or conduction. This property led to the earlier designation of the function as the *total heat* or *heat content*; but as shown by the following example, it might equally well be called the "total geopotential" or "geopotential content":

In an adiabatic ascent with negligible velocity change, $gdZ = -dH$. If the enthalpy change in such a process be expressed as a function of the temperature change (dT), the lapse rate may be ascertained; for a perfect gas, since $dH = dE + d(PV)$ by definition, and $dE = c_v dT$, we have $dH = c_v dT + R dT = (c_v + R) dT = c_p dT$, whence the adiabatic lapse rate is $dT/dZ = -g/c_p$.

The so-called "stream-function" $gZ + c_p T$, which has recently been included in routine daily meteorological reports, is in a limited sense the equivalent of the quantity $gZ + H$ of equation (3); the limitation lies in the fact that $c_p T$ evaluates only the enthalpy of the dry air component of the atmosphere (relative to that for air at 0° abs.). Thus the stream-function does not take into account the very important source of energy which exists in the water vapor component of atmospheric air; whereas, the enthalpy function, properly interpreted as the aggregate enthalpy of the air and vapor, takes into account the energy of both components. As an illustration, for air at 10° C. and 2,000 meters height, with a mixing ratio of 10 g./kg., the geopotential is 19 joules per gram and the enthalpies of the air and the vapor are respectively 83 and 27 joules per gram of air (relative to dry air at 200° K.), the vapor thus contributing nearly 30 percent additional energy. The data on the relative enthalpy of water vapor in the accompanying table should facilitate the extension of the stream-function to include the vapor energy and so enhance appreciably the effectiveness of that function in meteorological analyses. If the vapor energy be included in the stream-function, this function becomes highly conservative for *all* adiabatic processes, including those involving adiabatic saturation by evaporation.

Another useful property of this function is the following: Since the enthalpy is a function of the state, it may be employed as one of a pair of coordinates with which the properties and property changes of a fluid may conveniently be represented graphically. Energy may then be ascertained directly, *simply by reading the enthalpy scale*, avoiding the evaluation of integrals or "areas" (such as $\int VdP$, $\int PdV$ or $\int TdS$). An "enthalpy-entropy diagram" has therefore become the primary practical indicator diagram of the engineer. The writer has prepared such an enthalpy-entropy diagram for the air-vapor mixtures that exist in the atmosphere.

The particular data listed in the table are the enthalpy

of saturated water (h_f , joules per gram) and saturated water vapor (h_g) at the indicated temperatures; the change of enthalpy (h_{fg} , or the familiar "latent heat," L) for vaporization at those temperatures and the corresponding saturation pressures; the enthalpy of ice (or snow, h_i) and of saturated vapor (h_g) at 0° C. and below, and the change of enthalpy (h_{ig}) for sublimation at such temperatures. The symbols are those currently employed by the engineering physicist and recently standardized by the thermodynamics subcommittee of the American Standards Association. As the internal energy component of the enthalpy function ($E+PV$) is capable only of relative evaluation, any evaluation of the enthalpy function must also be relative. In order to avoid negative magnitudes, the quantities in the table are relative to an arbitrarily-assigned value of zero for ice at -73° C. (200° K.); the units employed, joules per gram, seem particularly suitable for meteorological purposes. The values in the Keenan-Keates Tables are in B. t. u. per lb. and relative to a zero for water at 0° C.

Inspection of the table shows that h_{ig} exhibits a relatively minor variation; the mean value of about 2838 j./g., or 677.9 cal. per gm., agrees well with the value of 677 cal./gm. frequently quoted in meteorological literature. The quantities h_g and h_{fg} are almost linear functions of temperature within the given temperature range:

$$h_g = 2969 + 1.81 t^\circ \text{C.} \\ = 2477 + 1.81 T^\circ \text{K. j./g.} \quad (4)$$

$$h_{fg} = 2502 - 2.38 t^\circ \text{C.} \\ = 3142 - 2.38 T^\circ \text{K. j./g.} \quad (5)$$

From the Clapeyron equation, $h_{fg} = VT \frac{dP}{dT}$, and the gas constant $PV/T = 0.461$ for the vapor, we have

$$h_{fg} = 3142 - 2.38T = 0.461T^2P^{-1}(dP/dT),$$

that is,

$$\frac{dP}{P} = \frac{3142}{.461} T^{-2} dT - \frac{2.38}{.461} \frac{dT}{T},$$

or

$$\ln(P/P_0) = 6820(1/T_0 - 1/T) - 5.26 \ln(T/T_0)$$

The agreement with equation (1) is quite satisfactory in view of the general approximations employed. However, some disagreement is apparent between equation (5) and the relation

$$L = 594.9 - 0.51 t^\circ \text{C. cal./gm.}, \\ = 2520 - 2.1 t^\circ \text{C. joules/gm.},$$

often given in the literature (see, e. g., Brunt, *Physical and Dynamical Meteorology*, 2d ed., p. 58).

The indicated value of 1.81 j./g. deg. or 0.435 cal./gm. deg. for $d h_g/dT$ does not agree closely with the values of about 0.465 that have frequently been quoted in meteorological literature for the specific heat of water vapor at constant pressure; but in view of the reliability of these most recent data, it is to be regarded as the more probable figure.

The remaining columns of the table contain the entropy, in joules per gram, ° Kelvin (or ° C. abs.) of

saturated liquid (s_f) or ice (s_i) and of saturated vapor (s_g), and the associated changes of entropy for evaporation (s_{fg}) or sublimation (s_{ig}). The values are again relative to an arbitrarily assigned value of zero for ice at -73° C. Although it may not seem conventional to employ such specific magnitudes of the relative entropy in meteorological computations relating to ice, liquid, or vapor and their mixtures with air, the writer has found it very convenient to do so in computations associated with wet-adiabatics.

Thermal properties of water—solid, and saturated liquid and vapor phases +50° to -40° C.

[Values based on results of international research as tabulated by Keenan and Keates, 1936, but with magnitudes in metric units and relative to zero values of enthalpy and entropy for ice at 200° K., or -73° C.]

Temperature °C	Saturated vapor pressure mb.	Saturated vapor density gm./cu. m.	Enthalpy, joules/gm.			Entropy, joules/gm. ° K.				
			h_f	h_{fg}	h_g	s_f	s_{fg}	s_g		
50	123.3	83.1	676	2,383	3,059	2.49	7.37	9.86		
48	111.5	75.6	668	2,388	3,056	2.46	7.43	9.89		
46	100.9	68.8	659	2,393	3,052	2.44	7.49	9.93		
44	91.1	62.5	651	2,398	3,049	2.41	7.56	9.97		
42	82.0	56.6	643	2,402	3,045	2.39	7.62	10.01		
40	73.7	51.2	634	2,407	3,041	2.36	7.68	10.04		
38	66.2	46.3	626	2,412	3,038	2.33	7.75	10.08		
36	59.4	41.8	618	2,416	3,034	2.30	7.82	10.12		
34	53.2	37.6	610	2,421	3,031	2.28	7.88	10.16		
32	47.5	33.8	601	2,426	3,027	2.25	7.95	10.20		
30	42.43	30.4	592	2,431	3,023	2.22	8.02	10.24		
28	37.78	27.3	584	2,436	3,020	2.19	8.09	10.28		
26	33.65	24.4	576	2,441	3,016	2.17	8.16	10.33		
24	29.82	21.8	567	2,446	3,013	2.14	8.22	10.37		
22	26.40	19.4	559	2,450	3,009	2.11	8.30	10.41		
20	23.37	17.31	551	2,454	3,005	2.08	8.37	10.45		
18	20.61	15.37	543	2,459	3,002	2.06	8.44	10.50		
16	18.16	13.65	534	2,464	2,998	2.03	8.52	10.55		
14	15.98	12.09	526	2,468	2,994	2.00	8.59	10.59		
12	14.03	10.68	517	2,473	2,990	1.97	8.67	10.64		
10	12.28	9.41	509	2,478	2,987	1.94	8.75	10.69		
8	10.73	8.29	501	2,482	2,983	1.91	8.83	10.74		
6	9.35	7.27	492	2,487	2,979	1.88	8.91	10.79		
4	8.13	6.37	484	2,492	2,976	1.85	8.99	10.84		
2	7.05	5.56	475	2,497	2,972	1.82	9.07	10.89		
0	6.105	4.85	467	2,502	2,969	1.79	9.16	10.95		
	Over water	Over ice	Over water	Over ice	h_i	h_{ig}	h_g	s_i	s_{ig}	s_g
0	6.105	6.105	4.85	4.85	134	2,835	2,969	0.57	10.38	10.95
-2	5.27	5.17	4.22	4.14	129	2,836	2,965	0.55	10.45	11.00
-4	4.54	4.37	3.66	3.53	125	2,836	2,961	0.54	10.53	11.07
-6	3.90	3.69	3.17	3.00	121	2,837	2,958	0.52	10.61	11.13
-8	3.34	3.10	2.74	2.54	117	2,837	2,954	0.51	10.69	11.20
-10	2.86	2.60	2.36	2.14	113	2,837	2,950	0.49	10.78	11.27
-12	2.44	2.18	2.03	1.81	109	2,838	2,947	0.48	10.86	11.34
-14	2.07	1.80	1.74	1.51	105	2,838	2,943	0.46	10.95	11.41
-16	1.75	1.51	1.48	1.28	101	2,838	2,939	0.44	11.04	11.48
-18	1.48	1.25	1.26	1.06	97	2,839	2,936	0.43	11.12	11.55
-20	1.24	1.04	1.07	.892	93	2,839	2,932	0.41	11.21	11.62
-22		.854		.738	89	2,839	2,928	0.40	11.30	11.70
-24		.702		.612	85	2,839	2,924	0.38	11.39	11.77
-26		.578		.506	81	2,840	2,921	0.37	11.48	11.85
-28		.468		.414	77	2,840	2,917	0.35	11.58	11.93
-30		.381		.340	74	2,840	2,914	0.34	11.67	12.01
-32		.310		.279	70	2,840	2,910	0.32	11.77	12.09
-34		.250		.227	67	2,839	2,906	0.30	11.87	12.17
-36		.202		.185	63	2,839	2,902	0.29	11.97	12.26
-38		.163		.151	60	2,839	2,899	0.27	12.07	12.34
-40		.131		.122	56	2,839	2,895	0.26	12.17	12.43
-73					0	2,836	2,836	0.0	14.20	14.20

NOTES AND REVIEWS

W. E. KNOWLES-MIDDLETON. *Meteorological Instruments*. Toronto (University of Toronto Press), 1941. 213 pp., 160 figs.

This volume is the first general textbook on its subject in the English language to be published since Cleveland Abbe's *Treatise on Meteorological Apparatus and Methods* in the "Report of the Chief Signal Officer for 1887." The successive chapters cover the instruments commonly used to measure atmospheric pressure, surface temperature (air, soil, and water), humidity, precipitation and evaporation, surface wind (speed and direction), upper-air wind velocity, the motions and heights of clouds and the sizes of cloud or fog droplets, and the duration of sunshine. A concluding chapter is devoted to meteorographs and radiosondes. Numerous references to the literature are included throughout the book.

Charles B. Tuch, the designer of the barometer cistern that bears his name, died in Washington, D. C., on August 1, 1941, at the age of 91, and was buried in Arlington National Cemetery with military honors.

During the early years of the Weather Bureau, first under the Signal Corps (in which he enlisted on April 11, 1879) and later under the Department of Agriculture, Mr. Tuch was engaged in the instrument work of the Bureau, where his faithful and conscientious services were of the greatest value. He became the head instrument maker; and had charge particularly of the repair, calibration, and shipping of mercurial barometers, in which he excelled anyone else. Prior to about 1890, the only *self-recording* instrument at any of the field stations

was the Gibbon anemometer register; as barographs, thermographs, and other self-recording instruments were introduced later, their care was also assigned to Mr. Tuch.

The two mercurial barometers with which each station has always been equipped were perhaps the most important of all the instruments at the stations. Mr. Tuch's chief duties were to maintain the readings of these at the highest possible accuracy. At that time the barometers were of the so-called "Fortin" type, having glass and boxwood cisterns with chamois skin bags permitting of the adjustment of the mercury level. The maintenance of these instruments involved not only the cleaning and frequent renewal of the cisterns, but also the fitting of new glass barometer tubes, which had first to be filled with vacuum-distilled mercury of the highest possible purity. Before issue for use, each instrument had to be carefully compared, by readings extending over several days, with the primary standards of the Bureau, and its scale adjusted until the correction for instrumental error was found to be no greater than four thousandths of an inch. The experience gained in this work led to the invention of the so-called Tuch barometer cistern, in which the perishable boxwood chamois skin container for the mercury was replaced by a sturdy metal cylinder with mercury-tight plunger to adjust the level of the mercury to the ivory point for a reading.

Mr. Tuch remained connected with the Weather Bureau until 1916.

METEOROLOGICAL AND CLIMATOLOGICAL DATA FOR NOVEMBER 1941

[Climate and Crop Weather Division, J. B. KINCEP in charge]

AEROLOGICAL OBSERVATIONS

By HOMER D. DYCK

Mean surface temperatures for November were from 2° to 4° F. above normal over most of the country with the exception of an area in the central Gulf States which was slightly below normal.

At 1,500 meters above sea level the 5 a. m. resultant winds for November were from directions to the south of normal over most of the country with the exception of Texas and Oklahoma, where they were from directions to north of normal. Although a comparison of the morning resultant winds at 3,000 meters was not possible for the lake region, the Ohio Valley, California, and Nevada, the winds at this level were from directions to the south of normal over most of the rest of the United States with the exception of New Mexico, Oklahoma, and Texas, where resultant winds were to north of normal. At 5,000 meters a good comparison of the 5 p. m. resultant winds with the corresponding 5 a. m. normals was not possible over most of the country. It may be noted, however, that these afternoon winds were from directions to north of normal over California and the southern plateau region and from south of normal over the central Great Plains.

At 1,500 meters resultant wind velocities were above normal over the northern half of the country, west of the Rockies generally and over the central Gulf States, and below normal elsewhere. At 3,000 meters a comparison, of wind velocities, was not possible over the lake region, the Ohio Valley, California, and Nevada, but resultant velocities were below normal generally over the southeast, the southern plateau and extreme northern Montana and

above normal elsewhere. At 5,000 meters all stations where a comparison of the 5 p. m. resultant velocities with the corresponding 5 a. m. normals was possible, had above normal velocities. These stations were located over the western half of the country and the central and southern Great Plains.

A correlation between mean surface temperature departures and deviations from normal resultant wind directions is evident. At both 1,500 and 3,000 meters there are areas where a turning to northward of normal took place which have the same general shape as the area where below normal surface temperatures occurred. These areas where the winds turned to northward are, however, displaced somewhat to westward of the area where below-normal temperatures were recorded. The remainder of the country recorded above-normal temperatures and resultant winds to south of normal generally.

When the 5 p. m. resultant directions are compared to the corresponding 5 a. m. resultant directions, a turning to northward during the day is noted at the 1,500 meter level over the lake region, the upper Mississippi Valley, Alabama, Georgia, and South Carolina, while a turning to southward occurred over the rest of the country generally. At the 3,000 meter level no well marked pattern of change was evident; it may be noted, however, that the number of stations where turning to southward during the day occurred was about double the number where the opposite shift occurred.

The 5 p. m. resultant velocities at 1,500 meters were lower than the corresponding 5 a. m. velocities over the Atlantic States, the Ohio Valley, the Gulf States, and the northwest generally and were above the morning velocities