METHODS FOR COMPUTING THE BOILING TEMPERATURE OF WATER AT VARYING PRESSURES

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Four functions for computing boiling temperature are tested and the results are compared to data from the *CRC Handbook of Physics and Chemistry*.

Boiling has been described as a violent form of evaporation that occurs when the saturation (or equilibrium) vapor pressure is equal to the total atmospheric pressure (Glickman 2000). But atmospheric pressure varies with height (e.g., it is lower in Denver, Colorado, than it is in Miami, Florida), so the boiling temperature should also vary with height. It ought to be a simple matter to manipulate the known thermodynamic relationships to derive an equation describing the boiling point of water at a given atmospheric pressure. One such relation is the closed form of the Clausius–Clapeyron equation:

$$e_s = e_0 \exp\left[\frac{l_\upsilon}{R_\upsilon}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right], \quad (1)$$

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where e_s is the saturation vapor pressure (Pa), e_0 is the vapor pressure at the triple point of water (611.12 Pa), l_υ is the latent heat of vaporization (equal to 2.5008×10^6 J kg^{-1} at 0°C, decreasing by about 10% as temperature increases to 100°C), R_υ is the individual gas constant for vapor (461.2 J kg^{-1} K^{-1}), T_0 is the temperature at the triple point (273.16 K), and T is the temperature (K) (Miller 2015). This equation can be recast to show the relationship between total atmospheric pressure and the boiling temperature of water by

$$p_B = e_0 \exp\left[\frac{l_\upsilon}{R_\upsilon}\left(\frac{1}{T_0}-\frac{1}{T_B}\right)\right], \quad (2)$$

where p_B is the total atmospheric pressure at which the water is boiled (Pa) and T_B is the boiling temperature of water (K) at pressure p_B. By inverting this equation, we can then compute the boiling temperature at any given pressure. After about five steps, we arrive at

$$T_B = \frac{1}{\frac{1}{T_0}-\frac{R_\upsilon}{l_\upsilon}\ln\left(\frac{p_B}{e_0}\right)}. \quad (3)$$

There is a slight problem in using this expression to compute all boiling temperatures: l_υ is *not* a constant (e.g., Court 1985; Henderson-Sellers 1984, 1985; Rogers and Yau 1989). It varies with temperature

(in this case T_B), which implies that we would need to compute l_v before computing T_B. To do that, we need to know T_B first. There are numerical methods for closing this loop, but another method that yields results with a relatively small error is to simply use an average value of l_v in the known range of temperatures. The purposes and motivation of the research described in this paper were 1) to try three variations on the latent heat of vaporization (one a constant and two different functions of temperature) and apply these toward computing boiling temperature as a function of the total atmospheric pressure in the Clausius–Clapeyron equation and 2) to determine a direct function of total atmospheric pressure for computing boiling temperature. For the purposes of this research, the boiling temperatures listed in Lide (2006) were considered correct.

METHODS AND RESULTS. *Method 1: Constant l_v.* In the first method, the boiling temperature of water was computed for the pressures between mean sea level pressure (MSLP; 1,013.25 hPa) and the lower pressure (high elevation) limit shown on most skew T–log$p$ diagrams (100 hPa) using (3) and the value of l_v at 50°C (2.3893×10^6 J kg^{-1}) from Table 1 (Tsonis 2007). This value of l_v was chosen for two reasons: 1) its corresponding temperature is midway between the known boiling temperatures at MSLP and at pressures near the top of the stratosphere and 2) doing so made it possible to determine the accuracy of the results when only a rough approximation of the parameter is used. The results are shown in Table 2.

Table 2 also shows boiling-point data taken from Lide (2006) and a summary of the differences between the boiling points computed from (3) and the boiling points taken from Lide (2006). Bias (column 5 of Table 2) was defined as computed value minus the Lide (2006) value. Accepting the values taken from Lide (2006) as "correct," the error values in column 6 of Table 2 were then computed by

$$\text{Error} = \text{abs}\left[\frac{(\text{Computed value}) - (\text{Lide 2006 value})}{(\text{Lide 2006 value})}\right] \times 100\%, \quad (4)$$

where the Lide (2006) values used in the denominator were first converted to the absolute scale.

These results indicate that, to within less than half a percentage point (mean error 0.33%) and about 1.15°C (mean bias), the Clausius–Clapeyron equation can be used to estimate the boiling point temperature of water in pressures typical of Earth's lower atmosphere, even when using a rough estimate of the value of the latent heat of vaporization.

Table 1. Latent heat of vaporization for water. Some values have been interpolated from available data (Tsonis 2007).

Temperature (°C)	l_v (10^6 J kg^{-1})
50	2.3893
45	2.3945
40	2.4062
35	2.4183
30	2.4300
25	2.4418
20	2.4535
15	2.4656
10	2.4774
5	2.4891
0	2.5008
−5	2.5128
−10	2.5247
−15	2.5366
−20	2.5494
−25	2.5622
−30	2.5749
−35	2.5890
−40	2.6030
−45	2.6189
−50	2.6348

Table 2. Comparison of boiling temperature values computed from the Clausius–Clapeyron equation with constant l_v (method 1) to values from Lide (2006). Elevations correspond to the *U.S. Standard Atmosphere* (NASA 1962, 1966, 1976).

Pressure (hPa)	Elevation (m)	Computed value (°C)	Lide (2006) value (°C)	Bias (°C)	Error (%)
1,013.25	0	100.76	100.00	0.76	0.20
1,000	111	100.41	99.63	0.78	0.21
900	988	97.59	96.71	0.88	0.24
800	1,947	94.49	93.51	0.98	0.27
700	3,010	91.04	89.96	1.08	0.30
600	4,203	87.14	85.95	1.19	0.33
500	5,570	82.63	81.34	1.29	0.36
400	7,180	77.26	75.88	1.38	0.40
300	9,157	70.57	69.11	1.46	0.43
200	11,766	61.56	60.07	1.49	0.45
100	15,787	47.22	45.82	1.40	0.44

Method 2: Linearly varying l_v. The second method used a linear function for l_v, and then used the computed value of l_v in (3) in an error-reduction loop to compute boiling temperature as a function of total atmospheric pressure. The linear function is

$$l_v = l_{v0} + l_{v1}T, \tag{5}$$

where l_v is the latent heat of vaporization at temperature T (J kg^{-1}), l_{v0} is its value at 0°C (2.5008×10^6 J kg^{-1}), l_{v1} is the slope of a linear function (−2,369), and T is the temperature (°C) (Miller 2015). This equation is described in greater detail in Rogers and Yau (1989). In this method, l_{v0} and l_{v1} were considered fixed constants, not variables to be determined. An error-reduction loop involving variable coefficients was employed in the third method, described below.

In the error-reduction loop for method 2, a first-guess temperature was used to estimate the value of l_v with (5), and the inverted Clausius–Clapeyron equation (3) was then used with the estimated l_v to compute the boiling temperature at a selected pressure. The resulting temperature was then substituted into the latent heat relationship (5), yielding an updated value of l_v, and the process was repeated. This was continued for each selected pressure level until the resulting boiling temperature from (3) and the guess temperature used for l_v in (5) were within 0.01°C. This method was used to compute boiling temperatures for the same pressures listed in Table 2, then compared to boiling point temperatures from Lide (2006). The results are shown in Table 3 and indicate a mean bias of about 6.45°C and a mean error of about 1.78% in the applicable range of pressures. Both of these are larger than the results described in Table 2. That is, by substituting this functional value of l_v for the fixed value (in an attempt to improve the prediction of boiling point temperature), the results got worse, not better.

Table 3. Comparison of boiling temperature values computed with linear-function l_v (method 2) to values from Lide (2006). Bias and error are as defined in text.

Pressure (hPa)	Computed value (°C)	Lide (2006) value (°C)	Bias (°C)	Error (%)
1,013.25	110.22	100.00	10.22	2.74
1,000	109.74	99.63	10.11	2.71
900	106.01	96.71	9.30	2.51
800	101.97	93.51	8.46	2.31
700	97.56	89.96	7.60	2.09
600	92.67	85.95	6.72	1.87
500	87.14	81.34	5.80	1.64
400	80.72	75.88	4.84	1.39
300	72.93	69.11	3.82	1.15
200	62.77	60.07	2.70	0.81
100	47.23	45.82	1.41	0.44

Method 3: Second-order polynomial function for l_v. The third method started with determining a new function for the latent heat of vaporization, by comparing the saturation vapor pressures derived from the Clausius–Clapeyron equation (which assumes temperature-dependent *variable* values of l_v) to the saturation vapor pressures derived for the same temperature using an advanced form of the equation (which assumes a *fixed* value of l_v, called l_{v0}):

$$e_s = e_0 \exp\left[\frac{l_{v0}}{R_v}\left(\frac{1}{T_0}-\frac{1}{T}\right)-\left(\frac{c-c_p^{\text{vapor}}}{R_v}\right)\ln\left(\frac{T}{T_0}\right)+T_0\left(\frac{1}{T_0}-\frac{1}{T}\right)\left(\frac{c-c_p^{\text{vapor}}}{R_v}\right)\right], \tag{6}$$

where e_0 is the reference pressure (611.12 Pa), l_{v0} is the latent heat of vaporization at 0°C (2.5008×10^6 J kg^{-1}), R_v is the individual gas constant for water vapor (461.2 J kg^{-1} K^{-1}), T_0 is the reference temperature at the triple point of water (273.16 K), T is the in situ temperature (K), c is the specific heat of liquid water at 0°C (4,215 J kg^{-1} K^{-1}), and c_p^{vapor} is the specific heat of water vapor at constant pressure (1,844.8 J kg^{-1} K^{-1}) (Miller 2015). Equation (6) can be derived analytically by referring to Rogers and Yau (1989), combining Eqs. (2.10) and (2.14) in their text, and integrating the result. It is also listed in Brock and Richardson (2001) in a slightly different form.

The values of l_v as a function of temperature between 0° and 100°C (in 1°C increments) were estimated by

- computing saturation vapor pressure with (1), which uses the temperature-dependent variable value of l_v, starting with a first-guess value of l_v;
- computing saturation vapor pressure with (6), which uses the fixed value of l_{v0}; and
- adjusting the variable value of l_v used in (1) to systematically minimize the difference between the two vapor pressures.

Henderson-Sellers (1984) derived a second-order function to compute l_v as a function of T. With this example in mind, a second-order polynomial ($R^2 \approx 1.0000$ and $\sigma = 49.11$ J kg^{-1}) was fitted to the results of the error-reduction calculations described above, taking the form

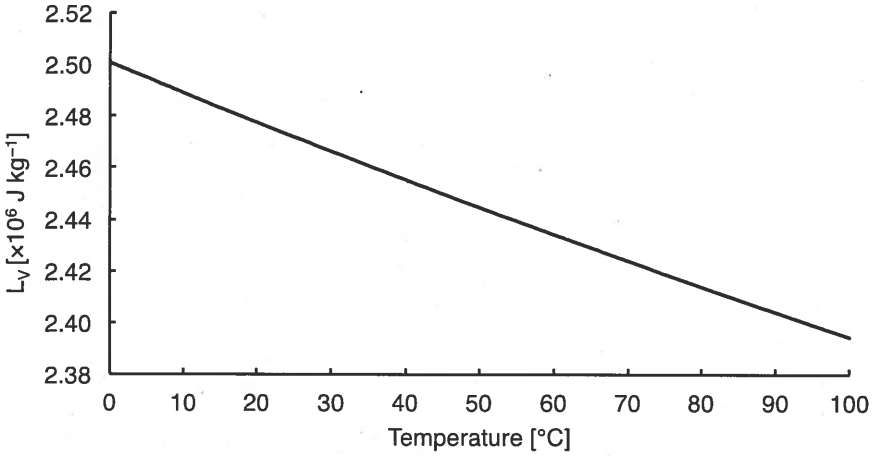

FIG. 1. Latent heat of vaporization as a function of temperature, computed by method 3.

$$l_v = l_{v0} + l_{v1}T + l_{v2}T^2, \quad (7)$$

where l_v is the latent heat of vaporization (J kg^{-1}); l_{v0} is the new zeroth-order coefficient (2.5007×10^6), l_{v1} is the new first-order coefficient (−1,173.7723), l_{v2} is the second-order coefficient (1.1315), and T is the temperature (°C). [A first-order fit, similar to (5), yielded an R^2 of 0.9992.] Figure 1 shows the shape of the nearly linear function, and Table 4 summarizes the comparison between the computed values of l_v and those listed in Tsonis (2007). The mean bias between 0° and 50°C is 0.0309×10^6 (J kg^{-1}) (meaning the computed values are slightly high), and the mean error is 1.28%, indicating that (7) yields values of l_v that are probably serviceable for most meteorological applications (e.g., calculations of water vapor mixing ratio and integrated precipitable water). The rate of error growth in the available range of data suggests that the error at 100°C is about 5%, which is also probably sufficient for most meteorological applications.

From here, a second error-reduction loop was used to compute the boiling temperature as a function of pressure. In this loop, a first-guess temperature was used to compute the latent heat term using (7), and (3) was then used to compute the boiling temperature at a selected pressure. The resulting temperature was then substituted into the latent heat relationship (7), and the process was repeated. This was continued until the resulting boiling temperature from (3) and the guess temperature used for l_v in (7) were within 0.01°C. This method was used to compute boiling temperatures for pressures between 50 and 1,080 hPa, in 1-hPa increments. The results were stored in a file with two columns (one containing pressure and the other boiling temperature) and are plotted in Fig. 2.

Sample values of the boiling temperature computed with (7) in the error-reduction loop were compared to boiling point temperatures taken from Lide (2006), which is summarized in Table 5. The bias and error

TABLE 4. Comparison of l_v computed via (7) and those listed in Tsonis (2007).

Temperature (°C)	Computed l_v (10^6 J kg^{-1})	Tsonis (2007) l_v (10^6 J kg^{-1})	Bias (10^6 J kg^{-1})	Error (%)
100	2.3944			
95	2.3992			
90	2.4041			
85	2.4090			
80	2.4139			
75	2.4189			
70	2.4240			
65	2.4291			
60	2.4342			
55	2.4395			
50	2.4447	2.3893	0.0554	2.32
45	2.4500	2.3945	0.0555	2.32
40	2.4554	2.4062	0.0492	2.05
35	2.4608	2.4183	0.0546	2.27
30	2.4663	2.4300	0.0363	1.49
25	2.4719	2.4418	0.0301	1.23
20	2.4775	2.4535	0.0239	0.97
15	2.4832	2.4656	2.4656	0.71
10	2.4889	2.4774	0.0115	0.46
5	2.4948	2.4891	0.0057	0.23
0	2.5007	2.5008	−0.0001	0.004

values shown in columns 4 and 5 of Table 5 indicate the results are still warm relative to the Lide (2006) values, but to a smaller degree than the results of the calculations that used the fixed value of l_v (Table 2), and to a much lesser degree than the calculations using the linear-functional l_v (Table 3). The mean bias is 0.31°C, and the mean error in the range of pressures shown is 0.08%.

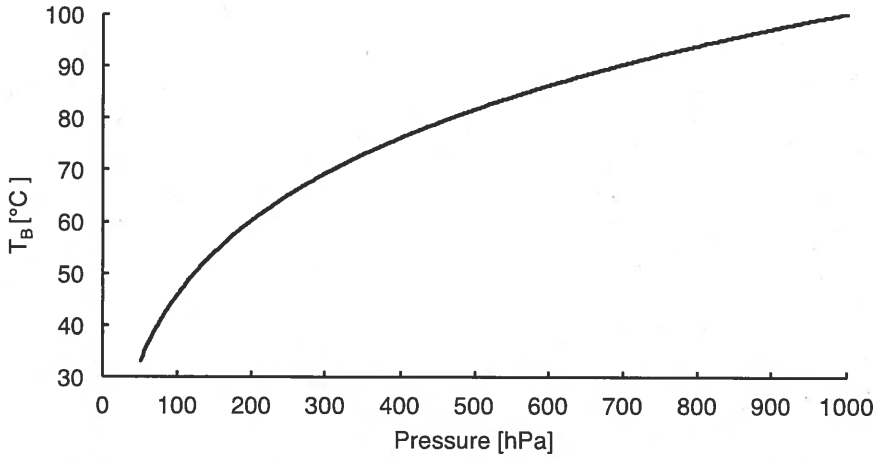

FIG. 2. Boiling temperature as a function of pressure, computed by method 3.

Method 4: Polynomial fits to method 3 results. The fourth and final method fitted a fifth-order polynomial, with $R^2 = 0.9998$ and $\sigma = 0.2377$°C, to the boiling pressure and temperature data in the file derived with the third method, using pressure as the independent variable and eliminating latent heat altogether:

$$T_B = a + bp_B + cp_B^2 + dp_B^3 + ep_B^4 + fp_B^5, \quad (8)$$

where T_B is the boiling temperature (°C), p_B is the pressure (hPa), and a–f are coefficients shown in Table 6. Lower-order polynomials yielded lower values of R^2, which is to be expected. A first-order fit yielded an R^2 value of 0.9236, and a second-order fit had a value of 0.9874. The fifth-order fit was judged a reasonable balance between quality of fit and usability, although additional work could certainly be done to fit higher-order polynomials. Different functions (a natural log function would be the logical choice) could also be tried in some future work.

Sample values of the boiling temperature computed with (8) were compared to boiling point temperatures taken from Lide (2006) and are summarized in Table 7. The bias and error values shown in columns 4 and 5 of Table 7 indicate this function is also slightly warm relative to the Lide (2006) values. The mean bias is 0.25°C, and the mean error in the range of pressures shown is 0.09%.

TABLE 5. Comparison of boiling temperature values computed with second-order function l_v (method 3) to values from Lide (2006).

Pressure (hPa)	Computed value (°C)	Lide (2006) value (°C)	Bias (°C)	Error (%)
1,013.25	100.50	100.00	0.50	0.13
1,000	100.12	99.63	0.49	0.13
900	97.16	96.71	0.45	0.12
800	93.92	93.51	0.41	0.11
700	90.32	89.96	0.36	0.10
600	86.27	85.95	0.32	0.09
500	81.61	81.34	0.27	0.08
400	76.10	75.88	0.22	0.06
300	69.28	69.11	0.17	0.05
200	60.19	60.07	0.12	0.04
100	45.87	45.82	0.05	0.02

SUMMARY AND CONCLUSIONS. Boiling is an extreme form of evaporation that occurs when the saturation vapor pressure is equal to the total atmospheric pressure (Glickman 2000). The Clausius–Clapeyron equation (1) was recast to describe the boiling point (2) and solved for boiling temperature (3). Since one term in the equation is the latent heat of vaporization l_v, which is a function of temperature, one can either use an approximation of l_v to compute boiling temperature T_B at a given pressure P_B or use a temperature-dependent functional expression of l_v and proceed through an error-reduction loop. The purposes and motivation of

TABLE 6. Coefficients for fifth-order polynomial fit for boiling temperature as a function of pressure (method 4).

Coefficient	Value
a	20.682
b	0.3151
c	−0.000079207
d	1.1999×10^{-6}
e	-9.178×10^{-10}
f	2.7412×10^{-13}

this research were 1) to test one constant value and two temperature-dependent functional expressions for l_v in the Clausius–Clapeyron equation and 2) to derive a simple polynomial function, with atmospheric pressure as the independent variable, to compute boiling temperature. Values of boiling temperature as a function of pressure as reported in Lide (2006) were used as the standard by which all four methods were judged. Results are summarized in Table 8.

The first method used the value of l_v valid for 50°C and obtained results that were correct to within a mean error of 0.33% and a mean bias of 1.15°C for pressures typical of Earth's troposphere and lower stratosphere. The second method used the linear expression for l_v described by (5) (Rogers and Yau 1989), and the result was an even greater disagreement between computed values of T_B from (3) and those listed in Lide (2006), with a mean bias of about 6.45°C between MSLP and 100 hPa (indicating computed values of the boiling temperature were too warm) and a mean error of about 1.78%.

The third method began by deriving a new, second-order, temperature-dependent polynomial (7) for l_v. The new function for l_v yields a mean latent heat error of 1.28% between 0° and 50°C when compared to those listed in Tsonis (2007), and a probable error at 100°C of about 5%. An error-reduction loop was used to compute the boiling temperature as a function of pressure, wherein a first-guess temperature was used to compute the latent heat coefficient using the second-order polynomial shown in (7), and (3) was then used to compute the boiling temperature at a selected pressure. The resulting temperature from (3) was then substituted into the latent heat relationship (7), and the process was repeated until the resulting boiling temperature from (3) and the guess temperature used for l_v in (7) were within 0.01°C. This method was used to compute boiling temperatures for pressures between 50 and 1,080 hPa, in 1-hPa increments. This method for computing T_B showed a warm bias (mean value 0.31°C between MSLP and 100 hPa) compared to Lide (2006) and a mean error about 4 times smaller than those associated with computed values of T_B that used the constant value of l_v.

The fourth method fitted a fifth-order polynomial (eliminating l_v and making P_B the sole independent variable) to the boiling temperatures resulting from the third method (8). The polynomial shows an R^2 value of 0.9998 and fit standard deviation of 0.2377°C. Computed values of T_B using the polynomial were associated with a mean bias of 0.25°C and a mean error of 0.09% when compared to Lide (2006).

Table 7. Comparison of boiling temperature values computed with fifth-order polynomial (method 4) to values from Lide (2006).

Pressure (hPa)	Computed value (°C)	Lide (2006) value (°C)	Bias (°C)	Error (%)
1,013.25	100.34	100.00	0.34	0.09
1,000	99.93	99.63	0.30	0.08
900	97.12	96.71	0.41	0.11
800	94.08	93.51	0.57	0.16
700	90.41	89.96	0.45	0.12
600	86.14	85.95	0.19	0.05
500	81.41	81.34	0.07	0.02
400	76.10	75.88	0.22	0.06
300	69.56	69.11	0.44	0.13
200	60.24	60.07	0.17	0.05
100	45.38	45.82	−0.44	0.14

Table 8. Comparison of mean bias and error between MSLP and 100 hPa for methods tested to compute boiling temperature.

Method	Mean bias (°C)	Mean error (%)
1. Constant l_v in (3)	1.15	0.33
2. Linear l_v (5) in (3)	6.45	1.78
3. Second-order l_v (7) in (3)	0.31	0.08
4. Fifth-order polynomial in P_B (8)	0.25	0.09

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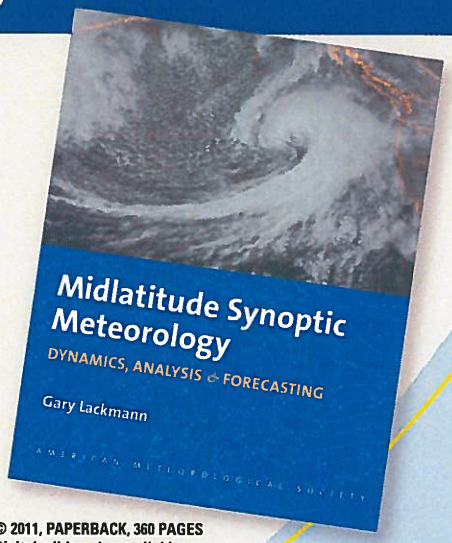

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