ICE.

The Missouri River at Omaha, Nebr., closed for the second time on the 8th, and at St. Joseph, Mo., on the 7th. It remained closed at Omaha at the end of the month, with ice about 8 inches in thickness, but opened on the 22d at St. Joseph. The river was also closed at Kansas City, Mo., from the 9th to the 16th, inclusive, and at Boonville, Mo., from the 11th to the 21st, inclusive.

The Mississippi River was frozen as far down as Hannibal, Mo., on the 8th, opening at Hannibal on the 23d, when the gorge above the Wabash Bridge broke. A gorge also existed above the Eads Bridge at St. Louis from the 13th to the 16th, inclusive. No ice of consequence was observed below the mouth of the Ohio River.

There was a decided increase during the month in the thickness of the ice in the Missouri and upper Mississippi rivers and in the Red River of the North, the increase amounting to more than 100 per cent. At the end of the month there was somewhat more ice than at the end of January, 1908.

There was also considerable ice in the Columbia River during the first half of the month, and at times the river was closed almost to the mouth of the Willamette River.

In the MONTHLY WEATHER REVIEW for December, 1908, mention was made of the floods of that month in the rivers of Arizona, and the following brief report thereon was made by Mr. L. N. Jesunofsky, official in charge of the local office of the Weather Bureau at Phoenix, Ariz.:

Heavy precipitation occurred generally over the northern and central sections of the Territory on December 15, 16, and 17, 1908, resulting in a rapid run-off in the Verde, upper Salt, and Little Colorado rivers. The precipitation over their drainage areas averaged about 1.85 inches during the three days mentioned. During the twenty-four hours ending with 8 a. m., December 16, the Salt River at Tempe, Ariz., had risen 6 feet and was still rising rapidly. The Gila River rose slightly. At 8 a. m., December 17, the gage at Tempe read 11.5 feet, and the river was then falling after reaching a crest stage of 12 feet at 5:30 a. m. of that date. The crest past Roosevelt, on the upper Salt River, at 1:30 a. m., and over the lower Verde River at about 2:30 a. m., December 17. During this entire period the Gila River rose only 2 feet.

On the 16th warnings were sent out by telegraph that a flood stage of 12 feet would be reached by midnight of the same date, and the crest of exactly 12 feet past at 5:30 a. m., December 17. By 8 a. m., December 18, the river at Tempe had fallen to 6 feet, and by 8 a. m., December 19, to 3.5 feet, the Gila River remaining at a low stage.

About the same time the heavy rains in the upper watershed of the Little Colorado River congested that stream and its tributaries to such an extent that on the 16th the water rose rapidly some 25 or 30 feet in the vicinity of Winslow and St. Joseph, Ariz., washing away the railroad tracks for some miles. The damage resulting from these washouts amounted to about $8,000. Very little, if any, damage resulted from the floods in the Salt and Gila rivers, and the total damage did not amount to more than $10,000 or $12,000. The property saved thru the warnings was valued at about $3,000.

These floods in the Salt River Valley, altho not of great extent, were the greatest since the establishment of the Arizona River and Flood Service in May, 1907, and thus far excellent results have followed the forecasts of floods and marked rises in the streams whose beds are practically dry during six months of the year.

The highest and lowest water, mean stage, and monthly range at 207 river stations are given in Table IV. Hydrographs for typical points on seven principal rivers are shown on Chart I. The stations selected for charting are Keokuk, St. Louis, Memphis, Vicksburg, and New Orleans, on the Mississippi; Cincinnati and Cairo, on the Ohio; Nashville, on the Cumberland; Johnsonville, on the Tennessee; Kansas City, on the Missouri; Little Rock, on the Arkansas; and Shreveport, on the Red.—*H. C. Frankenfield, Professor of Meteorology.*

SPECIAL ARTICLES, NOTES, AND EXTRACTS.

THE PRESSURE OF SATURATED VAPOR FROM WATER AND ICE AS MEASURED BY DIFFERENT AUTHORITIES.

By CHARLES F. MARVIN, Professor of Meteorology. Dated December 10, 1908.

Dr. Nils Ekholm has recently published (1)[1] the results of a very notable study by him of the maximum pressures of aqueous vapor at different temperatures, as deduced from the observations of all the best authorities. While the present short article on the subject is essentially a review of Doctor Ekholm's paper, yet some details are added from a desire to set forth briefly the present status of our knowledge of this subject. Ekholm has not himself attempted to directly measure vapor pressure, but has brought together the results of the work of many others and has endeavored to eliminate as far as practicable various recognized as well as heretofore neglected minor errors. After harmonizing certain discrepancies and correcting all known errors as far as possible, Ekholm reduces the observations to a homogeneous series of vapor pressures for the whole range of temperature from —50° C., where the pressure is so small it can scarcely be measured, to 365° C., with a corresponding pressure of 200 atmospheres. Ekholm then seeks to represent this long series of observed temperatures and pressures by a single mathematical equation, the form of which is based upon the recognized thermo-dynamic relations between temperature and vapor pressure, as far as these have been set forth by various writers.

The following summary gives briefly the observational data utilized by Exholm:

[1] Heavy-faced numbers in parentheses refer to the bibliography at the end of this article.

Regnault.—The measurements by this great authority (2) were made at the College of France between 1840 and 1845, at a time when exact thermometry was almost unknown outside of Regnault's own laboratory, and when the instruments of precision and the multitude of conveniences commonly found in modern laboratories were quite unknown. Nevertheless, Regnault's classic work still constitutes the basis of all vapor pressure tables in common use. He covered a range of temperatures from —30° to +230° C., making in all nearly one thousand separate determinations that in point of skill and care bestowed upon them and in general accuracy of the results are unsurpassed. A similar work done independently by Magnus in Germany fully confirmed the observations by Regnault.

Broch.—Regnault did not escape the commission of certain technical errors in his work, which have been pointed out by Moritz and others, and later, when modern thermometry and manometry had been precisely defined, it became necessary to apply certain small systematic corrections to Regnault's observations. A recomputation with this object in view was very carefully effected by Broch (3) in 1881 at the International Bureau of Weights and Measures, and his tables of pressures from —30° to +101° C., are now probably in more general use by meteorologists than any other tables.

The principal source of trouble in Regnault's observations results from the fact that below 100° C. all his temperature readings were made on the so-called normal-mercury-in-glass thermometers. Regnault himself knew that the scale of temperatures thus obtained differed slightly from that of the air thermometer, and from the hydrogen scale, but the corrections between 0° and 100° doubtless seemed small to him, and more especially was it difficult to establish their value with the same exactitude as in the remainder of his work. Regnault therefore published his results without these small corrections, nor was their application attempted by Broch. The latter collected all of Regnault's observations between —30° and 101° C. (over 500 in number) and combined them into 21 groups, from which he deduced mean values of the pressure at selected points on Regnault's scale of temperatures, i. e., at 10°, 20°, 30°, etc. Broch gives these final values only in the Regnault units of temperature and pressure. They can not therefore be directly and easily compared with other data exprest in standard units. While it is probably impossible at the present time to accurately transform Regnault's values to others on the hydrogen scale of temperatures, they can, however, be easily reduced to normal-mercury-thermometer temperatures and to manometric units under standard gravity by utilizing the data already given by Broch; the method of procedure would be as follows. Broch gives for each of his 21 groups and means of pressures observed by Regnault the difference between the observed value and that calculated by Broch's formula, but all are exprest in Regnault's units. Now, assuming that these differences will be sensibly the same if we deal with values in normal units and adding or subtracting the differences from Broch's tabulated values, I get the values given in Table 3, column 2, under the heading: Regnault by Broch.

Additional remarks on the reduction to the hydrogen scale will be made further on.

Juhlin, Marvin.—Between 1890 and 1891 Juhlin (4) in Upsala and Marvin (5) in Washington independently determined vapor pressures, especially over subcooled water and over ice at temperatures from 0° to —50° C. The observations of both these investigators bring out prominently the difference called for by theory between the vapor pressure over ice, below zero, and the pressure over undercooled water or water at temperatures below its freezing point. Juhlin and Marvin also made some measurements at moderate temperatures above freezing. Ekholm gives the values of Marvin above freezing a prominent place in his adopted series of vapor pressures, and for this purpose the original observations (33 in number, from 32° to 80° F.) were combined into four values at 0°, 10°, 20°, and 30° C. It seems to me that the method Ekholm employed to effect this combination is not the best, and apparently introduces some small errors. Moreover, as Marvin's vapor pressures above freezing have never been published, except in the Annual Report of the Chief Signal Officer, U. S. Army, for 1891, and are not accessible to many students, they are now reprinted in Table 1, and a method is given for deducing values at even temperatures of 10°, 20°, and 30° C. that seem likely to be more accurate than those adopted by Ekholm.

Marvin's original observations on the pressure of vapor over water at temperatures above freezing were made in groups at approximately 5-degree points on the Fahrenheit scale from 35° to 80°, the pressures being measured in millimeters and all necessary reductions made to normal air thermometer temperatures and normal manometer units. Table 1 contains the individual determinations, the mean group-temperatures in Fahrenheit and centigrade units, and the mean pressures. The last column (Marvin minus Broch) gives the departures of Marvin from the values calculated by Broch's formula, which latter differ slightly from Regnault's observed values as reduced by Broch and given in Table 3, column 2.

It will be noticed that the departures, Marvin—Broch, increase progressively and with marked regularity from zero upward. In order to deduce from these results corresponding representative values at the even 10°, 20°, and 30° points on the temperature scale, it seems to the writer that the best way to combine such observations is to plot the departure, and draw a smooth curve thru them as is shown in Chart XI fig. 1. The figures near each plotted point give the number of observations on which that mean value depends, and aid in weighting the respective points. With Broch's formula and this curve of differences we get the values of pressure resulting from Marvin's observations, as shown in Table 2.

TABLE 1.—*Marvin vapor-pressure observations. Above freezing.*

	Temperature.		Pressure.	Marvin minus Broch.
	°F.	°C.	*Mm.*	*Mm.*
			*4.558	
			4.595	
			*4.533	
			4.562	
			4.554	
			4.586	
			4.575	
			*4.580	
			4.584	
			4.566	
Means of 10 observations (melting ice)	32.00	0.00	4.5683	—0.0004
	34.96		5.164	
	34.95		5.171	
Means of 2 observations	34.96	1.65	5.168	+0.02
	39.44		6.166	
	39.68		6.256	
	40.07		6.297	
	39.70		6.217	
Means of 4 observations	39.72	4.29	6.234	+0.041
	44.78		7.554	
	44.75		7.595	
	44.94		7.614	
Means of 3 observations	44.82	7.12	7.588	+0.061
	49.22		8.947	
	49.86		9.154	
	49.87		9.153	
	50.09		9.239	
Means of 4 observations	49.76	9.87	9.123	+0.062
	54.91		11.080	
	55.18		11.163	
	55.04		11.123	
	55.23		11.151	
Means of 4 observations	55.09	12.82	11.129	+0.122
	59.41		12.993	
	59.80		13.178	
	59.78		13.143	
	59.17		12.904	
	59.99		13.246	
Means of 5 observations	59.63	15.35	13.093	+0.132
	64.76		15.696	
	64.59		15.581	
	64.91		15.764	
Means of 3 observations	64.75	18.19	15.680	+0.166
	69.91		18.747	
	69.58		18.541	
	69.88		18.732	
Means of 3 observations	69.79	20.99	18.673	+0.218
	74.65		21.957	
	75.08		22.268	
	74.93		22.171	
Means of 3 observations	74.89	23.82	22.132	+0.219
	80.05		26.279	
	79.84		26.106	
Means of 2 observations	79.94	26.64	26.192	+0.275

* The braces connect observations made at different times, but with one and the same piece of apparatus.

TABLE 2.—*Marvin's reduction of his own observations of vapor pressure.*

Temperature.	Broch.	Marvin minus Broch.	Marvin.	Marvin as used by Ekholm.
°C.	*Mm.*	*Mm.*	*Mm.*	*Mm.*
0	4.5687	0.000	4.5683	....
5	6.507	+0.033	6.540	....
10	9.140	+0.078	9.218	9.216
15	12.674	+0.130	12.804	....
20	17.363	+0.186	17.549	17.533
25	23.517	+0.250	23.767	....
30	31.510	+0.315	31.825	31.781

Thiesen and Scheel: 1893.—The observations by these authorities (6) were made at the "Reichsanstalt" or German National Bureau of Standards, and, altho the range of temperatures is very limited (−11° C. to +25° C.), yet the determinations were made with the utmost care and every pains taken to eliminate, as perfectly as possible, the influences of errors. Only two sets of measurements were made below the freezing point, namely, one set at −6.561° C., in which the authors state that the water in the apparatus was frozen, and one set at −11.334° C., for which the water was probably still liquid; but the original paper is not entirely definite as to whether this water was, or was not, frozen. The pressure does not correspond very well with Marvin and Juhlin, but the probability seems to be, and I have assumed that, the water was *not* frozen.

Wiebe: 1893.—The determinations by Wiebe (7) were also made at the Reichsanstalt, and with every possible care; they are given in Table 3, column 3. As in the case of Thiesen and Scheel, the range of temperatures was very limited, but at a higher point on the scale; namely, from 82° C. to 100° C. Thus, Wiebe's measurements serve to fix the values near the boiling point, while Thiesen's fix the values at and near the freezing point.

Landolt and Börnstein: (8).—In the new edition of the Landolt–Börnstein Physikalisch–Chemische Tabellen (Berlin, 1905, pages 118–122), Regnault's and Broch's vapor pressure tables have been recomputed with corrections and adjustment of the values so as to incorporate the results of Juhlin, Marvin, Thiesen and Scheel, and Wiebe, and finally to reduce temperatures to the hydrogen scale. Just how all these results have been effected and what equations and constants have been employed, are not explained.

Regnault gave numerous comparisons of his mercury thermometers with the gas thermometer at temperatures above the boiling point, where the differences are large, and altho he states that these thermometers read lower than the gas thermometer between zero and 100° C., yet carefully determined differences were not published. In discussing this subject Wiebe computed the corrections to Regnault's thermometers between 0° and 100° C., by using an equation the constants of which were determined by observations above 100° C. Ekholm seems also to have followed this course in the reductions he made of Regnault's observations between zero and 100° C., but eventually Regnault's results within these limits were not used by him.

Pressures at high temperatures.—In addition to the above-mentioned observations made by Regnault at temperatures above the boiling point, several other series have been executed with more or less exactness and the range of temperatures considerably extended, so as to include especially the condition in the neighborhood of the so-called critical temperature and pressure; that is, at about 365° C. and a pressure of 200 atmospheres.

Three series of observed pressures at high temperatures are available, as follows:

Ramsay and Young (9).—These cover the range of temperatures from 120° to 270° C.; that is, about 40° higher than observed by Regnault, and probably mark the upper limit of conditions under which steam is useful in operations of practical steam engineering.

Battelli (10), *Cailletet and Colardeau* (11).—These two remaining series of vapor pressure determinations were made in Italy and France, respectively, and extend the range to the critical temperature and pressure beyond which the customary distinctions between liquid and vapor state no longer exist.

Those who have consulted Regnault's original memoirs will recall that for purposes of interpolation he plotted with great accuracy many of his observations (about one-third, he himself says) directly upon a great copper plate, with centimeter lines engraved thereon, and provided with a device to accurately subdivide these centimeter squares. Regnault's tabulated results, as well as the modern revised tables at high temperatures based thereon, are derived directly from these curves. Ekholm calls attention to important discordances between results from the curves and observations not plotted, and he revises all the observations combining them at 10° points on the temperature scale; the latter he reduces to standard units and the pressures to normal gravity.

We need not comment further upon this large mass of valuable observational data, and in order to enable the reader to estimate for himself the relative merits of the different investigations we give in Table 3 a summary of all the observations on a strictly comparable basis. Ekholm's accepted values appear in column 6. He regarded Juhlin's values over ice too large on account of a small capillary error and subtracted .027 millimeter from each to correct for the same. Column 3 contains the values thus obtained, which are almost identical with Marvin's values. Ekholm's accepted values in column 6 are the mean of these two after altering Marvin's readings by .001 or .002 millimeter to eliminate a supposed effect due to the unequal pressure of the mercury vapor in the manometer. At +10° C., also, Juhlin's and Marvin's values are identical. At 20° and 30° C. Marvin's values only are used by Ekholm. All these results are given a weight of 10. None of the Regnault data below 100° C. is used, nor the values of Thiesen and Scheel. The latter, however, agree so nearly with those used, that their omission or inclusion, unless excessively weighted, would make very little difference. Observations are wanting above 30° C. until we come to Wiebe's results from 80° to 100° C. These are given a weight of 400. Above 100° C. Regnault's values are weighted 10; Ramsey and Young, Battelli, and Cailletet and Colardeau, each 1. Ekholm constructs from this material the set of values given in Table 3, column 6, which may be considered as observational results accepted by him for further study.

Holborn and Henning.—The work of these writers (12) has only recently been published and was not available to Ekholm, but their results are included here for comparison with others. This series of measurements was made at the Reichsanstalt and embraces a range of conditions from 50° to 200° C. It is needless to say that all the precautions known to modern science were observed, to eliminate and to correct for influences of errors from all sources.

As in the case of Regnault's observations the pressures were measured with a great mercurial manometer, having in this case a total height of 12 meters, and extending upward thru several stories of the laboratory. A notable feature of this investigation is the use of electrical resistance thermometers in the determination of temperature. Elaborate care was taken to establish accurately the constants of these platinum resistance thermometers, and the relation of the temperatures thus obtained to those of the nitrogen thermometer. The temperatures were all finally reduced to the thermodynamic scale. The results of this investigation are given in column 10 of Table 3.

For completeness we add the following values, exhibiting our present knowledge of the relation between the hydrogen and the thermodynamic scales. We quote from a letter of Dr. Edgar Buckingham of the Bureau of Standards:

According to D. Berthelot (Travaux et Memoires, Bureau International du Poids et Mesures, Tome XIII, p. 101), the constant-volume hydrogen thermometer, with an initial pressure of 1,000 millimeters of mercury at the ice point, reads lower than the thermodynamic scale by the following amounts:

° C.	° C.
−100	+0.008
0	0.000
+ 40	−0.00055
+ 60	−0.00052
+100	0.000
+200	+0.003
+300	+0.007
+400	+0.013

It is probable that in the present state of thermometry the differences of the two scales are absolutely negligible.

TABLE 3.—*Maximum pressure of aqueous vapor over water and ice as found by different authorities.*

1	2	3		4		5		Ekholm.						10
								6		7	8		9	
Temperature.	Regnault by Broch.*	Juhlin by Ekholm.		Marvin.		Thiesen and Scheel.		Accepted observations.		Weights.	Calculated and adopted.		Observed minus the calculated.	Holborn and Henning.*
	Water.	Ice.	Water.	Ice.	Water.	Ice.	Water.	Ice.	Water.		Ice.	Water.		
°C	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*	*Mm.*		*Mm.*	*Mm.*	*Mm.*	*Mm.*
−50		0.029		0.030				0.030		10	0.031		− 0.001	
−40		0.094		0.100				0.096		10	0.100		− 0.004	
−30	0.3538	0.284		0.284				0.285		10	0.293		− 0.008	
−20	0.8210	0.779		0.781				0.782		10	0.788		− 0.006	
−10	2.0272	1.969	2.165	1.961	2.156		2.136	1.963	2.165	10	1.968		− 0.005	
−5				3.009	3.164	3.050					3.033			
0	4.5686		4.572		4.568		4.579		4.571	10		4.604	− 0.033	
+5					6.540							6.566		
10	9.0888		9.216		9.218				9.216	10		9.234	− 0.018	
15					12.804		12.778					12.817		
20	17.3645				17.549		17.520		17.533	10		17.568	− 0.035	
25					23.767		23.683					23.797		
30	31.5309				31.825				31.781	10		31.873	− 0.092	
40	54.8970											55.401		
		11 Wiebe.												
50	91.9326											92.641		92.30
60	148.9160											149.575		149.19
70	233.4807											233.932		233.58
75	288.5221											289.850		289.0
80	354.8948		355.50						355.50	400		355.438	+ 0.06	355.1
85	433.5677		433.68						433.68	400		433.757	− 0.08	433.5
90	525.2701		526.11						526.11	400		526.021	+ 0.09	525.8
93	587.9580											588.842		588.7
95	633.4407		634.18						634.18	400		634.095	+ 0.08	634.0
97	681.9741											682.199		682.1
99	733.4244											733.291		733.3
100	759.7944		760.00						760.00	∞		760.000	0.00	760.00
101	784.2350													
	12 Regnault.	13 Ramsay and Young.		14 Battelli.		15 Cailletet and Colardeau.								
110														
120	1491.00		1484						1490.4	11		1488.8	+ 2.1	1488.9
125							1672		1672.0	1		1737.6	− 65.6	1744.5
130	2026.48		2019		2043				2027.2	12		2024.4	+ 2.8	2025.6
140	2708.30		2694						2707.0	11		2707.6	− 0.6	2709.5
145					3129				3129.1	1		3113.0	+ 16.1	3115.3
150	3567.36		3568				3572		3567.8	12		3565.8	+ 2.0	3568.7
160	4636.55		4652						4638.0	11		4629.8	+ 8.2	4633.
170	5349.77		5937						5948.6	11		5932.9	+ 15.7	5937.
175							6688		6688.	1		6685.5	+ 2.5	6689.
180	7531.76		7487†						7527.7	11		7511.7	+ 16.0	7514.
185					8360				8360.	1		8416.9	− 56.5	8417.
190	9408.63		9403						9408.1	11		9405.1	+ 3.0	9404.
200	11651.53		11625		11635		11628		11646.4	13		11655.2	− 8.8	11647.
210	14292.48		14240						14287.7	11		14306.6	− 18.9	
220	17341.30		17365						17343.5	11		17406.6	− 63.1	
225							19076		19076.	1		19140.2	− 64.2	
230	20924.47		20936		(20738)				20925.5	11		21004.9	− 79.4	
240			25019						25019.	1		25155.8	− 136.8	
250			29734				29792		29763.	2		29914.6	− 151.6	
260			35059						35059.	1		35339.9	− 280.9	
270			41101						41101.	1		41493.6	− 392.6	
275							45144		45144.	1		44864.0	+ 280.0	
300							65512		65512.	1		64991.4	+ 520.6	
310					(78290)				78290.	1		74740.5	+(3549.5)	
325							92416		92416.	1		91427.7	+ 988.3	
335					(106814)				106814.	1		104048.	+(2766.)	
350							127300		127300.	1		125044.	+ 1855.	
360					140815				140815.	1		141486.	− 671.0	
365					149707		152380		151043.5	2		150078.	+ 965.5	

All pressures are exprest in standard manometric units.

* The values in column 2 are for temperatures on the Regnault normal mercury-in-glass thermometer; those in column 10 are on the thermodynamic scale. All other values are on the hydrogen scale.

† Dr. A. D. Risteen in "The Locomotive," April, 1907, p. 187, a pamphlet published by the Hartford Steam Boiler Inspection and Insurance Company, Hartford, Conn., calls attention to an obvious mathematical error in respect to this value in the original paper. The correct value is 7478.

VAPOR PRESSURE FORMULA.

Many attempts have been made to formulate a vapor pressure equation based on what is known of the thermodynamic relations between the pressures and temperatures of vapors, and a considerable degree of success has been realized in certain cases. The calculated values on the whole, however, do not agree with the observed pressure with sufficient accuracy to satisfy many demands. The numerical tables for pressure of aqueous vapor now in general use are derived either directly from observations or from equations having different forms and different constants for different parts of the temperature range.

Ekholm has endeavored to embrace the entire range of pressures within the scope of a single equation. He recognizes, however, the differences which both experiment and theory call for between vapor pressures over ice and over water.

Ekholm has not limited himself to one form of equation, nor to a single set of constants, but gives such a variety of results as to leave the reader a little puzzled as to which to select as the best.

For a preliminary study he tries the following equation, derived from studies by Clapeyron and Clausius:

$$\frac{dp}{dt} = \frac{Er}{T(s-\sigma)} \qquad (1)$$

p=vapor pressure over fluid water in dynes per square centimeter; T=absolute temperature; E=the mechanical equivalent of heat; r=latent heat of evaporation; and s and σ=the volume of a unit weight of vapor and water, respectively; all in C. G. S. units.

Not satisfied with the results obtained from this equation, Ekholm sought by trial to find some sufficiently simple func-

TABLE 4.—*Showing pressures accepted by Ekholm as derived from various observers, with the differences in millimeters and in percentages between various equations and authorities*

Temperature.	Accepted pressures by Ekholm.		Accepted pressures minus equation (18), (Ekholm).		Accepted pressures minus equation (20), (Ekholm).		Accepted pressures minus equation (37). (Clausius.)		Accepted pressures minus Broch, —30° to 100°. minus Regnault, 100° to 230°.		Accepted pressures minus Landolt and Börnstein, 1905.		Accepted pressures minus Holborn and Henning, 1908.	
	Pressure.	Weight.												
°C.	Mm.		Mm.	%	Mm.	%	Mm.	%	Mm.	%	Mm.	%	Mm.	%
—50	0.030	10	— 0.001	—3.33	±0.000	±0.00	+ 0.001	+3.33	...	...	— 0.004	—13.33	...	...
—40	0.096	10	— 0.004	—4.17	—0.002	—2.08	± 0.000	±0.00	...	...	— 0.009	— 9.38	...	...
—30	0.285	10	— 0.008	—2.81	—0.003	—1.05	+ 0.001	+0.35	— 0.095	—33.3	— 0.007	— 2.46	...	...
—20	0.782	10	— 0.006	—0.77	+0.004	+0.51	+ 0.009	+1.15	— 0.162	—20.7	— 0.005	— 0.64	...	...
—10	1.963	10	— 0.005	—0.26	+0.012	+0.62	+ 0.016	+0.82	— 0.188	— 0.6	— 0.011	— 0.56	...	...
0	4.571	10	— 0.033	—0.72	—0.008	—0.18	— 0.008	—0.18	+ 0.002	+ 0.04	— 0.008	— 0.18	...	...
+10	9.216	10	— 0.018	—0.19	+0.014	+0.15	+ 0.004	+0.04	+ 0.076	+ 0.08	+ 0.037	+ 0.40	...	...
20	17.533	10	— 0.035	—0.20	—0.001	—0.01	— 0.023	—0.13	+ 0.070	+ 0.04	+ 0.127	+ 0.73	...	...
30	31.781	10	— 0.092	—0.29	—0.059	—0.19	— 0.099	—0.31	+ 0.271	+ 0.09	+ 0.226	+ 0.71	...	...
40	...	...	...	...	...	...	...	...	...	...	...	...	...	...
50	...	...	...	...	...	...	...	...	...	...	...	...	...	...
60	...	...	...	...	...	...	...	...	...	...	...	...	...	...
70	...	...	...	...	...	...	...	...	...	...	...	...	...	...
80	355.50	400	+ 0.06	+0.02	±0.00	±0.00	— 0.05	—0.01	+ 0.63	+ 0.18	+ 0.03	+ 0.01	+ 0.40	+0.11
85	433.68	400	— 0.08	—0.02	—0.14	—0.03	— 0.17	—0.04	+ 0.49	+ 0.11	— 0.11	— 0.02	+ 0.18	+0.04
90	526.11	400	+ 0.09	+0.02	+0.03	+0.01	+ 0.04	+0.01	+ 0.64	+ 0.12	+ 0.11	+ 0.02	+ 0.31	+0.06
95	634.18	400	+ 0.08	+0.01	+0.05	+0.01	+ 0.06	+0.01	+ 0.52	+ 0.08	+ 0.09	+ 0.01	+ 0.18	+0.03
100	760.00	∞	± 0.00	±0.00	...	...	± 0.00	...	± 0.00	...	± 0.00	...	± 0.00	...
110	...	...	...	...	...	...	...	...	...	...	...	...	...	...
120	1490.4	11	+ 2.1	+0.14	...	...	+ 2.3	+0.16	— 0.9	— 0.01	— 0.6	± 0.00	+ 1.5	+0.01
125	1672.0	1	— 65.6	—3.93	...	...	— 65.3	—3.91	—71.9	— 4.31	—72.	— 4.31	—68.5	—4.10
130	2027.2	12	+ 2.8	+0.14	...	...	+ 3.2	+0.16	— 3.1	— 0.15	— 2.8	— 0.14	+ 1.6	+0.08
140	2707.0	11	— 0.6	—0.02	...	...	— 1.0	—0.04	—10.6	— 0.39	—11.0	— 0.41	— 2.5	—0.09
145	3129.1	1	+ 16.1	+0.50	...	...	— 16.5	—0.53	+ 3.6	+ 0.12	+ 4.1	+ 0.13	+13.8	+0.44
150	3567.8	12	+ 2.0	+0.06	...	...	+ 2.6	+0.07	—13.4	— 0.38	-13.2	— 0.37	— 0.9	—0.03
160	4638.0	11	+ 9.2	+0.17	+ 8.7	+0.19	+ 8.4	+0.18	—13.6	— 0.29	—13.0	— 0.28	+ 5.0	+0.11
170	5948.6	11	+ 15.7	+0.26	...	...	+ 15.2	+0.26	—13.1	— 0.22	—12.4	— 0.21	+12.0	+0.20
175	6688.	1	+ 2.5	+0.04	...	...	— 1.6	—0.02	—29.4	— 0.44	—29.0	— 0.43	+ 1.	+0.01
180	*7526.0	11	+ 16.0	+0.21	...	...	+ 14.5	+0.19	—19.5	— 0.26	—19.1	— 0.25	+13.	+0.17
185	8360.0	1	— 56.5	—0.68	...	...	— 58.7	—0.70	—93.2	— 1.11	—93.0	— 1.11	—57.	—0.68
190	9408.1	11	+ 3.0	+0.03	+ 2.7	+0.03	± 00.0	±0.00	—34.6	— 0.37	—33.9	— 0.36	+ 4.	+0.04
200	11646.4	13	— 8.8	—0.08	...	...	— 15.1	—0.13	—42.6	— 0.37	—41.6	— 0.36	+ 0.6	+0.01
210	14287.7	11	— 18.9	—0.13	...	...	— 28.5	—0.20	—37.1	— 0.26	—36.3	— 0.25	...	...
220	17343.5	11	— 63.1	—0.36	— 99.2	—0.57	— 78.1	—0.45	—46.9	— 0.27	—45.5	— 0.26	...	...
225	19076.	1	— 64.2	—0.34	...	...	— 83.1	—0.44	—21.0	— 0.10	—20.0	— 0.10	...	...
230	20925.5	11	— 79.4	—0.38	...	...	—102.1	—0.49	...	...	+ 0.5	+ 0.00	...	...
240	25019.	1	—136.8	—0.55	...	...	—168.7	—0.67	...	...	...	...	...	...
250	29763.	2	—151.6	—0.51	—197.1	—0.66	—202.3	—0.68	...	...	...	...	...	...
260	35059.	1	—280.9	—0.80	...	...	—340.9	—0.97	...	...	...	...	...	...
270	41101.	1	—392.6	—0.96	...	...	—472.0	—1.15	...	...	...	...	...	...
275	45144.	1	+280.0	+0.62	...	...	+188.0	+0.42	...	...	...	...	...	...
300	65512.	1	+520.6	+0.79	+194.5	+0.30	+351.3	+0.54	...	...	...	...	...	...
310	78290.	1	+(3549.5)	+4.53	...	...	+(3338.)	—4.27	...	...	...	...	...	...
325	92416.	1	+988.3	+1.07	...	...	+706.	+0.76	...	...	...	...	...	...
335	106814.	1	+(2834.)	+2.66	...	...	+(2401.)	+2.25	...	...	...	...	...	...
350	127300.	1	+ 1855.	+1.46	...	...	+1357.	+1.07	...	...	...	...	...	...
360	140815.	1	—671.	—0.48	...	...	—1286.	—0.91	...	...	...	...	...	...
365	151043.5	2	+965.5	+0.64	+ 1.5	+0.01	+280.	+0.19	...	...	...	...	...	...

* Corrected for error explained in foot note, table 3.

tion of pressure and temperature that would satisfy the observations, and for this purpose gave equation (1) the following form:

$$T\frac{d\log f}{dt}=\frac{E}{p(s-\sigma)},$$

which he considers better adapted to the requirements of the problem. After a number of transformations he obtains the following final form[1]:

$$\log f=\log 760+A\log\frac{a+t}{a+100}+B(\mathrm{li}\,x-\mathrm{li}\,X)+C(\mathrm{li}\,x-\mathrm{li}\,X),\quad(9)$$

where x and X are exponential functions of the absolute temperature of the following form:

$$\left.\begin{array}{l}x_t=10^{-k(a+t)}\\ X_t=10^{-l(a+t)}\end{array}\right\}\quad\ldots\ldots\ldots\ldots\ldots\ldots\ (16)$$

The expression "li" signifies the "integral logarithm" of the function between limits. Such an equation is troublesome in its computation because it requires the use of Ekholm's extended table of values of the integral logarithms.

The constants for formula (9) as derived by a least-squares analysis from the "accepted" data in column 6 of Table 3, are as follows for water vapor:

	Logarithm:	
k = 0.00281644		
l = 0.00821902		
A = 6.19373	0.791952	
B = 34.5868	1.538910	(18)
C = — 2.742	0.4381 neg.	
a = 272.6684° C.		

[1] We number the equations to agree with Ekholm's notations.

These constants, for water vapor substituted in equation (9) with necessary alteration for ice, to be explained later, give the calculated values in column 8 of Table 3, and have been adopted by Ekholm for the computation of extensive tables.

In equations (9) and (18) the constant a is the absolute temperature of the freezing point of water, that is to say the reciprocal of the coefficient of expansion for such gases as hydrogen, which, according to Broch, leads to the value a = 272.6684° C. It is frequently customary to use the whole number a = 273° C. Accordingly, Ekholm computed a new set of constants for equation (9), based on this latter value of a. These he designates (19), but they need not be given here as the pressures by the equation, do not differ from those by the old as much as a thousandth of a millimeter, except at high temperatures where the differences are very small.

Finally, Ekholm selects: (1) the value of f = 4.579 millimeters at 0° C. as measured with such elaborate care by Thiesen and Scheel; (2) the correspondingly carefully determined value f = 355.50 millimeters at 80° C. by Wiebe; and (3) the mean value f = 153378 millimeters at 365° C. from measurements of Battelli, Cailletet and Colardeau. With these three observations, still retaining a = 273° C. and two of the minor constants from set (19), new values of the constants A, B, and C were computed. The results, in full, are—

	Logarithm:	
k = 0.00281689		
l = 0.0076323		
A = 6.24086	0.795244	
B = 34.3398	1.535798	(20)
C = 7.33081	0.865151	
a = 273.00° C.		

We shall presently show more fully the differences between the observed pressures and the calculated values by these equations. Considering the close agreement realized and the labor involved in these tedious computations, we might have expected Ekholm to stop at this point. However, he also studies an additional equation (37) previously employed by Clausius, but with inaccurate constants derived from insufficient data. The original equation of Clausius is

$$\frac{P}{RT}=\frac{1}{v-a}-\frac{1}{\theta(v+\beta)^2} \qquad (21)$$

where P, T, and v are pressure, absolute temperature, and volume respectively; R and a are constants, and θ is a function of the temperature of which it is only stated that when $T = 0°$ C, $\theta = 0°$, and when $T =$ the critical temperature,

$$\theta = \frac{8}{27\,(\beta + a)}\,.$$

Important transformations are required to evaluate v and θ, but we shall not give these here. For the calculation of the constants of this equation Ekholm employs only three observations, namely: Thiesen and Scheel's value at freezing, $T = 273°$ C, $f = 4.579$ mm.; the pressure 760 mm. required by definition at the boiling point, $T = 373°$ C; and finally, the pressure and temperature at the critical point as deduced from the observations of Battelli and Cailletet and Colardeau, viz: $T = 637.65°$ C, $f = 150\,140$ mm. The equation resulting from these computations is designated "(37)" by Ekholm.

All the foregoing equations apply strictly to vapor over water. In Juhlin's experiments, a large number of measures were made with a differential manometer which gave directly the difference in pressure of vapor over water and vapor over ice at the same temperature. Arrhenius (12) has shown that these can be closely represented by the following simple equation:

$$\log f_{ice} = \log f_{water} + 0.004147\,t,$$

which Ekholm uses in connection with the equations already considered, and obtains values of vapor pressure over ice corresponding to the particular equation and constants employed for the calculation of f_{water}.

AGREEMENTS BETWEEN OBSERVED AND CALCULATED VALUES.

In Table 4 we give, first, in columns 1, 2, and 3, the observations accepted by Ekholm, Table 3, column 6, with their weights. In the remaining columns are given the differences between these accepted values and those calculated by the different equations. The differences are given in millimeters of pressure and also as percentages of the pressure. Since Broch's tables below 100° C have been and are still used so extensively in meteorological and physical work, and Regnault's tables above 100° in steam engineering problems, the differences between Ekholm and these authorities are included, likewise the differences from the Landolt and Börnstein tables, and from the Holborn and Henning tables.

In considering the relative merits of the several formulas we need to keep in mind that at low temperatures, say below 15° C., the inaccuracy in observations is chiefly caused by inaccuracy in the measurement of the *pressure*, as distinguished from the measurement of *temperature*. Errors in pressure of several thousandths, possibly of some hundredths of a millimeter can hardly be avoided in individual observations. At higher temperatures, on the other hand, the the limit of accuracy is chiefly dependent upon the errors of temperature measurements which, at the best, amount to at least one one-hundredth of a degree, and even some tenths of a degree at the highest temperatures.

The following values of dp when $dt = 0.1°$, will aid in interpreting Table 4:

Differences in pressure for a difference of 0.1° C.

Temperature (° C.)	—50	0	50	100	200	350
dp (in millimeters)	=0.003	0.033	0.46	2.71	24.4	153.

To bring out most forcibly the important information contained in Table 4 we require a diagram of the differences as shown in Chart XI, figs. 2 and 3, for example. To make the diagram clear in all its parts it has been necessary to use different scales for different portions. While the absolute values of the differences are very small at temperatures below zero, their percentage values are considerable. Whereas, between 80° and 100° the percentage differences are so small as to require an exaggerated scale to show them. The differences for some of the observations, above 100°, are so great they can not be included in the limits of a diagram that is suitable for the good observations.

The first generalization brought out from a study of Table 4 and the curves of Chart XI, fig. 2, is that below the freezing point the discrepancies between observation and calculation by equations (18) and (20), attain to a maximum of about 4 per cent at —40° C., but between this point and 30° C. the discordances are less than 1 per cent in every case, and in general are only a few tenths of a per cent. Between 80°C. and 100°C. the differences between the accepted and calculated pressures are only a few hundredths of a per cent, except those from Broch's table which run from one to two tenths of a per cent lower than Wiebe's observations. To bring out these small differences the scale of the diagram, Chart XI, fig. 2, between 80° C. and 100° C. is exaggerated as indicated by the numbering. The absence of observations between 30°C. and 80°C. leaves an element of doubt with respect to the exact value of vapor pressures for this region, so important to the meteorologist and physicist.

Above 100°C. the curves of Chart XI, fig. 3, up to 230°C., pass thru points determined from the observations and having a weight of 11 or more. From 230°C. to 270°C. the points refer to the observations by Ramsay and Young, and beyond this limit the points are located by the observations of Cailletet and Colardeau.

The first observation by Cailletet and Colardeau at 125°C. is widely discordant and falls outside the limits of the diagram. Several of the observations by Battelli, as at 145° and 180°C., and more notably those inclosed within parentheses in Tables 3 and 4 (namely, at 230°, 310°, and 335°C.) are all seriously discordant from the other observations, but, nevertheless, were included by Ekholm in his computations.

Those of Battelli's discordant differences that can be located within the limits of the diagram, Chart XI, fig. 3, are marked thus: $\left(\begin{matrix}B\\ \times\end{matrix}\right)$. These curves bring out in a striking manner the very close agreement below 230°C. between the observations of Regnault and Ramsay and Young; but above 270°C. the observations by Cailletet and Colardeau, and those of Battelli are not in equally close accord.

Regarding the several equations Ekholm remarks, on page 34:

The constants (18) or (19), as likewise (20), give so close an agreement between the observed and calculated values of f that there is no ground on which to prefer one over the other, and I have therefore retained the tables computed from (18), the more so since computations by Clausius' method, (see the next section), give very nearly the same values.

I think a close scrutiny of Table 3 and the curves of Chart XI will lead one to take exception to this conclusion. The vapor pressure at the freezing point has been determined with exceeding care by many observers. The values observed by Regnault, Juhlin, Marvin, Thiesen and Scheel agree within one-quarter of 1 per cent or less; whereas, equation (18) gives a value nearly 1 per cent higher than the average of the observations. Furthermore, the values calculated by (18) are systematically too high below 30°C., and also between 80° and

100°C., altho the differences have a small percentage value, especially in the latter case.

Tables of vapor pressure over the lower range of temperatures are used daily by meteorologists and they will hardly feel satisfied with a systematic discordance of the kind we have pointed out, which doubtless results in part at least from extending each individual equation over the extreme range of temperature.

The constants composing equations (20) do not result from a least-square computation that includes the whole series of observations, but depend chiefly on observations at temperatures 0°, 80°, and 365°C. Nevertheless, the calculated values below 60°C., especially over the meteorological range of temperatures, are in closer agreement with the observations than in the case of equation (18). Between 100° and 200°C. equation (20) gives values that agree with the observations quite as well as those from (18). Above 200° C. the differences are somewhat in doubt, as Ekholm has given values at only a few points. On the whole, the results favor the adoption of equation (20) rather than (18).

The constants of the Clausius equation (37) depend likewise on only three observations, in fact, only on two, namely, at 0°, and the critical temperature 364.65°C. since at the third point used, the boiling point, the pressure by definition must be 760.00 millimeters and this does not rank as an observation. This equation, nevertheless, agrees very closely with the observations and with (20) below +30°C. Between this point and 100°C. it runs appreciably higher than either (20) or (18), both of which seem higher than the observations.

The vapor pressures in Broch's tables below 0°C. must be regarded as pressures over undercooled water and are too high to be applicable to vapor over ice. Between 0° and 30°C. the values run slightly smaller, nearly one-tenth of 1 per cent, than Ekholm, but near 100°C. the discrepancies are larger. The Landolt and Börnstein table, edition 1905, is seriously discordant with Ekholm below —30°, but between —30° and 100°C. the agreement is closer than in the case of the Broch tables. All values are smaller than Ekholm's.

The Thiesen-Scheel and the Holborn-Henning observations from 0° to 100° are also smaller than the values calculated by Ekholm's formulas. We must, therefore, conclude that for meteorological work the values calculated by equations (9) and (18) and adopted by Ekholm for his extended tables are systematically slightly too high, as shown by all the best observations.

Above 100° we find the three Ekholm equations all in close accord with each other and the observations, up to about 200°C. Beyond this point the equations give values systematically and increasingly higher than the observations up to 270°C., at which temperature the observations by Ramsay and Young terminate. A marked discontinuity in the trend of the curves is required at this point to join with the observations by Cailletet and Colardeau, and we are compelled to regard the observations themselves between 270° and 365° C. as much less exact than for the lower temperatures.

The observations by Holborn and Henning are probably more accurate than any others over the range of temperatures from 100° to 200°C, and it is of great interest to notice how closely the results agree with Regnault's values determined over half a century earlier. The values last found are systematically smaller than Henning's reduction of Regnault's observations, but the maximum difference, exprest in temperatures, amounts to only 0.02° at any point; that is, less than 0.06 per cent at 140°C., and still smaller percentages at higher temperatures.

A further point of great interest is revealed from a comparison, in fig. 3, of the trend of the curves for Ekholm's equations, and that representing Holborn and Henning's work. These several curves follow each other from 80° to 200°C. in a very striking manner, and the inference is that if the Holborn and Henning values had been available to Ekholm his observed and calculated values would have shown a still closer agreement within this range of temperatures than is at present the case.

In conclusion it may be remarked that the systematic differences between observed and calculated values thruout what we may call the meteorological range of temperatures can not be accepted as entirely satisfactory. This, in some measure, must be caused by the effort to represent the pressures for the entire range of temperatures by one equation which is at least partly empirical. While, from the point of view of pure theoretical thermodynamics, only one equation is required, yet in the matter of practical application it is a question whether better results could not be secured by the use of two equations; one with constants, giving the best agreement with observations below 100°, due regard being paid below freezing to the difference between vapor over ice and over undercooled water, and the other equation adapted to conditions above 100°C. This alternative is, of course, preferable only on the assumption that the objections to the single equation can not be eliminated.

We have noticed a few errata in Ekholm's Table 7, namely: The differences in the last column should be, it seems, as follows:

At 0°, —.033 instead of —.031,
At 170°, +8.2 instead of +9.2,
At 340°, +2766. instead of +2834.

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