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Thermodynamic Properties of Substances as a Function of Reduced Temperature. I. Latent Heat. Vapor Volume and Vapor Pressure of Water

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In a previous article we have studied the relation between the ratio of orthobaric volumes and the reduced temperature of thirty diverse substances and shown that the relationship[1]

$$\ln \frac{V_g}{V_l} = \frac{k\,(1 - \tau^2)^m}{\tau^n} \tag{1}$$

where τ = "reduced" temperature T/T_{cr}; k, m and n are characteristic constants, holds within experimental limits.

In the present study we have made an attempt to express other thermodynamic properties in terms of reduced temperature in hope that it might throw some light on two problems: (a) latent heat as function of temperature alone; (b) the theory of corresponding states of van der Waals.

Dieterici very early recognized the importance of a detailed investigation of the relation between the reduced temperature and thermal properties of liquids for the final settling of the above two questions. He was concerned primarily with the ratio of volumes V_g/V_l, but his ideas can be applied to any particular "reduced" magnitude. Having established an approximate relationship between the inner latent heat and ln V_g/V_l he became interested in expressing L_{ev} as function of the temperature alone, in finding a functional relation between pressure and temperature and in advancing the theory of corresponding states. In one of his papers Dieterici suggested an approach to these problems as follows:[2] "According to the theory of corresponding states . . . the term ln V_g/V_l should have at equal reduced temperatures one and the same value for all 'normal' organic liquids. In reality this theory does not hold exactly. Still, if one plots ln V_g/V_l against τ one finds that the curves for normal substances deviate so little from each other that one can regard them all as identical. It would be of great interest to study ln V_g/V_l as function of reduced temperature and thus express the latent heat in terms of temperature alone.[3] This seems to be the most important problem. It is also certain that should this function be found, it would be a definite advance toward the fundamental question—the vapor pressure as function of temperature alone.[4] It is further possible that the deviations from the law of corresponding states are conditioned by the values of the critical constants of the different substances."

Since the proposed equation (1) expresses V_g/V_l with requisite accuracy, we feel justified, on the basis of the above quotation from Dieterici, to continue the investigation in order to see to what extent the previous findings could be applied to the relationship between the latent heat and temperature and to the theory of corresponding states.

In the first part of this paper we shall discuss the thermodynamic properties of one substance, namely, the latent heat, the vapor volume and the vapor pressure of water (the ratio V_g/V_l having been given before).

As far as we know there is no record of an attempt to correlate latent heat or vapor density with temperature, except for certain empirical equations with a large number of constants used by observers as a check on their measurements.

As to the vapor pressure, this property in its reduced form has been the subject of numerous investigations, the purpose of which was to find the possible causes of the deviations from the correspondence rule.[5] We shall discuss here the work of Cederberg, which is the most interesting of all.[6]

Cederberg's equation is really a modification of a formula by van der Waals and based on the theory of corresponding states

$$\ln P_{cr}/P_s = A\,\frac{1 - \tau}{\tau} \tag{2}$$

where τ is the reduced temperature; P_{cr} and P_s are the critical and saturation pressures, respectively, and A is a universal constant.

Van der Waals' equation holds only for an ideal substance; in actual cases A changes with temperature as well as from liquid to liquid.

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[1] H. A. Fales and C. S. Shapiro, THIS JOURNAL, **58**, 2418 (1936).

[2] C. Dieterici, *Ann. Physik*, **25**, 569 and especially 578 (1908).

[3] By substituting into Dieterici's equation: $L_{ev} = CRT \ln V_g/V_l + RT$ where C is a constant.

[4] By substituting into the Clapeyron–Clausius equation: $dp/dT = TL_{ev}(V_g - V_l)$.

[5] For a review of this subject and for the bibliography refer to Karl Jellinek, "Lehrbuch der phys. Chem.," Vol. I, ed. 1928, Verlag von Ferdinand Enke, Stuttgart, pp. 696–710.

[6] I. Cederberg, *Kgl. Svenska Vetenskapsakad.*, Arkiv Matematik, Astronomi och Fysik, **10**, No. 7 (1914) (in German).

Cederberg constructed his modification in accordance with several assumptions: first, that for every substance the factor A is passing through a minimum which lies at about 0.8 of critical temperature. This was found to be true for a large number of substances by Schames.[7] The second assumption by Cederberg was that for every substance the curve $A-\tau$ is symmetrical about the perpendicular to the abscissa erected from the "minimum" point. The third was that each branch of the $A-\tau$ curve is an exponential function of reduced temperature. All these suppositions were embodied in his expression

$$A = ab^{(\tau - y)^2} \quad \text{and} \tag{3}$$

$$\ln p_{cr}/p_s = 2.30\, ab^{(\tau - y)^2} \frac{(1-\tau)}{\tau} \tag{4}$$

where 2.30 is the modulus of the natural log; τ is the reduced temperature; a is the minimum value of A; y is the reduced temperature corresponding to this minimum and b is a constant characteristic for a given liquid.

Cederberg has tested about sixteen substances and found that the constants a, b and y vary with the chemical nature of the liquid. Thus a ranges from 3.1 for water to 2.77 for carbon tetrachloride; b varies from 2.4 for benzene to 1.58 for oxygen; y is nearly constant, the limits being 0.71 for oxygen and 0.80 for carbon dioxide.

Cederberg's calculations agree on the whole remarkably well with the observed pressures. For organic liquids the average deviation of his equation is about 0.3% for the entire range, which compares very well with the empirical equation of Biot having six constants and used by Young to check his pressure measurements[8]

$$\log_{10} P = a + b\alpha^{t-t_0} + c\beta^{t-t_0} \tag{5}$$

where a, b, c, α, β, and t_0 are characteristic for each substance.

For water the agreement is still better, the average deviation being less than 0.1% between melting point and critical point against the measurements of the Reichsanstalt.[6] As a final check Cederberg has calculated the pressure gradient for water and used it to calculate the latent heat which he then compared with the available measurements (100–180°) by Holborn and Henning of the Reichsanstalt. The difference averaged about 0.2% which, he felt, was within experimental limits.[9] In a few cases the discrepancy is considerable: thus for oxygen and for carbon dioxide the deviations at times reach 2% and are not evenly distributed. This may be partially due, according to the author, to inconsistencies in the experimental data, which were compiled from several short range observations by different experimenters.

In spite of all the good points mentioned above, Cederberg's equation did not receive universal recognition. The reason for this, we believe, is the following. The validity of the assumptions on which his idea is based may be open to question. Thus exceptions exist for which the constant A shows no minimum, but decreases steadily with temperature. These are helium and argon, as was shown by H. K. Onnes and C. Crommelin.[10] Also the symmetrical shape of the $A-\tau$ curve is doubtful because several liquids of those tested by Cederberg actually have shown a slight asymmetry. In such cases he considered the deviation to be due to errors in the critical pressure which he has changed arbitrarily so as to fit the requirement. Although the change in most cases was a fraction of a per cent., *i. e.*, within the limits of experimentation, this seems to us an artificial and inaccurate procedure. This will be clear from the following instances. In the case of hexane the critical pressure had to be changed by 0.4% before true symmetry could be attained, still the agreement was not as good as with other substances. In the case of water the asymmetry was very pronounced and the critical pressure was decreased from the observed value of 217.0 atm. (Reichsanstalt) to an arbitrary value of 216.3 atm., which gave the desired equality of the two branches and resulted in good agreement along the saturation line. One would expect the later measurements of P_{crit} to agree with Cederberg's value. On the contrary, the recent, very exact extrapolation from the latest observed pressures in the critical region leads to the value $P_{\text{cr}} = 218.7$ atm. (Keyes).[11] We see that the change lies in the opposite direction from that guessed by Cederberg.

Another objection to Cederberg's formula is its sensitivity to errors in critical temperature and in vapor pressure. Although he does not discuss this point, it seems to be obvious from the very form of his function

$$\ln P_{cr}/P_s = 2.30\, ab^{(\tau - y)^2} \frac{(1-\tau)}{\tau} \tag{4}$$

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[7] L. Schames, *Verh. Deutsch. Phys. Ges.*, **15**, 1017 (1913).

[8] S. Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

[9] I. Cederberg, *Physik. Z.*, **15**, 697 (1914).

[10] H. K. Onnes and C. Crommelin, *Leiden Commun.*, Nos. 120a, 119 and 124a.

[11] L. B. Smith, F. G. Keyes and H. T. Gerry, *Proc. Am. Acad. Sci.*, **69**, 137 (1934).

In this equation the term $\tau - y = \tau - 0.75$ approx. is very small and passes through zero at $\tau = 0.75$. An error of 0.1-0.5° in the critical temperature will influence it very much, particularly for substances with T_{cr} between 5 and 100°K. Since the term $(\tau - y)^2$ is an exponent, it is clear that any error in it will considerably affect the log and still more the calculated pressure itself, especially at high temperatures.

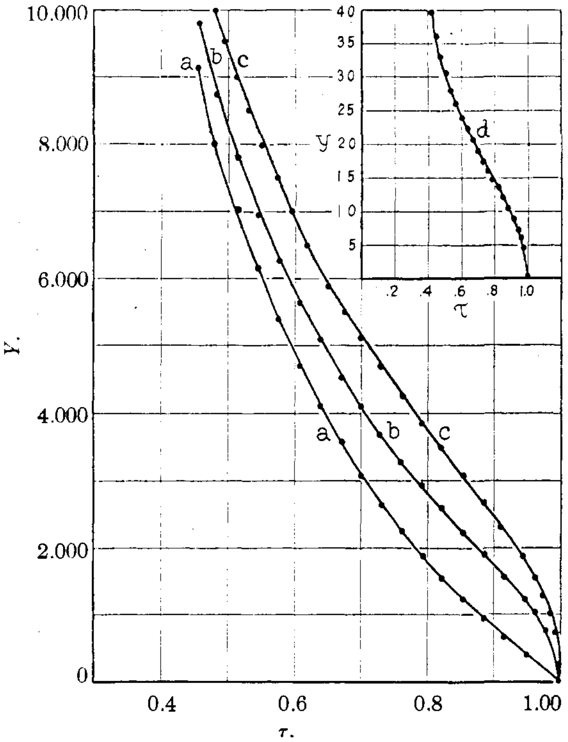

Fig. 1.—Curve *a*: $Y = \ln (P_{cr}/P_s) = k'[(1 - \tau^2)^{m'}/\tau^{n'}]$
Curve *b*: $Y = \ln(V_g/V_{cr}) = k''[(1 - \tau^2)^{m''}/\tau^{n''}]$
Curve *c*: $Y = \ln(V_g/V_l) = k[(1 - \tau^2)^{m}/\tau^{n}]$
Curve *d*: $Y = L_{ev}/T = S_{ev} = k'''[(1 - \tau^2)^{m'''}/\tau^{n'''}]$.

In addition the pressure data will have an influence on the deduced constants due to the fact that in order to find the exact location of the minimum point, y, one has actually to plot the curve A–τ, as was done by Cederberg. This requires *a priori* knowledge of observed data at high temperatures. Where these pressure data are scant or inaccurate the value of the constant y is uncertain and the formula becomes unreliable. This was the case with oxygen, where according to the author the experimental values of P were unreliable. The irregularities in the A–τ curve near the minimum point are thereby explained along with the resulting discrepancies between calculations and experiment.

The above listed defects of the Cederberg equation lead to the conclusion that another form of a "reduced" pressure equation would be desirable, one free from the stated objections and yet giving the same or better accuracy both for the pressures and for their derivatives with respect to temperature.

Such an equation when tested on a large number of substances undoubtedly would lead to a better understanding of the correspondence principle and its limitations. The same would be true not only of pressure, but of any other property as well.

As the first step toward the solution of this problem we have plotted on one and the same graph the thermodynamic properties of one substance against reduced temperature.

We have selected water as our test substance because of its importance and because its properties are measured very precisely between the melting point and the critical temperature. In Fig. 1 we show the curves, which follow each other in the order: $\ln P_{cr}/P_s$; $\ln V_g/V_{cr}$; $\ln V_g/V_l$ and L_{ev}/T, the last term being the entropy of evaporation.

All these curves coincide at $\tau = 1.000$, where the corresponding magnitudes assume the value zero. Inspection of the graphs reveals at once a striking similarity of form and although they represent different physical properties, they seem to belong to one and the same family. The question arises whether it is possible to express the curves as functions of form similar to equation (1).

As regards latent heat or, better, the entropy of evaporation L_{ev}/T, the similarity between its curve and that of $\ln V_g/V_l$ supports the view of other investigators, especially Dieterici[12] and MacDougall[13] that the two properties must be somehow related to each other, although it must be noted that these and other authors were unsuccessful in their attempts to find a satisfactory relationship.

On the basis of the similarity between the respective curves we have applied the proposed equation (1) in its original form to the entropy of evaporation

$$S_{ev} = \frac{L_{ev}}{T} = k''' \frac{(1 - \tau^2)^{m'''}}{\tau^{n'''}} \text{ cal. per mole} \qquad (6)$$

where S is the entropy of evaporation; L_{ev} is the molar latent heat; T and τ are the absolute and the reduced temperatures, respectively, and k''',

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(12) C. Dieterici, *Ann. Physik*, **25**, 569 (1908) and **62**, 75 (1920).

(13) F. H. MacDougall, THIS JOURNAL, **38**, 528 (1916), and **39**, 1229 (1917).

m''', n''' are constants different from those in equation (1).

To test this equation we have proceeded exactly as was described for the orthobaric densities.[1] Three observed values of L_{ev} at three different temperatures were used to calculate the constants. The three reference points were exactly the same as before. The observed values of L_{ev} were those of the Bureau of Standards.[14] Their measurements extend from 50 to 370° and agree with the measurements of the Reichsanstalt[15] within ±0.1% on the average for the same interval. The measurements of the Bureau of Standards are represented by an empirical equation[14] within ±0.04% in the interval 0–270° (see Table I).

In Table I we give details of our calculations. In successive columns will be found the values of the entropy of evaporation in calories per mole, the observed and calculated latent heats in calories per gram, the differences between observed and calculated values in calories and the same in per cent. The average deviation of the proposed equation is given at the bottom of the last column. The estimated tolerance of this equation and the accuracy of the Bureau of Standards formula also are given for comparison. At the bottom of Table I are given the two equations for reference.

The accuracy of the proposed equation is of the same order as in the case of orthobaric volumes.[1] The entropy of evaporation is entirely analogous to the term ln V_g/V_l, since the form of the function is identical for both. Therefore the deviation again will be composed of two terms: the error in T_{cr} which is the same as before and equal to 0.15% on the average and the error in latent heat measurement which is about 0.1% for water as stated above. The total estimated accuracy should be: $0.15 + 0.10 = 0.25\%$, which is exactly the figure obtained for the volume ratio. Of course near the critical point ($\tau = 0.95$ to 1.0) the error in T_{cr} will increase and the expression[6] is not expected to hold as was explained previously.[1]

In examining the last column of Table I we find that the maximum deviation between 60 and 350° is 0.25%, while the average deviation in the interval 40–350° is $\Delta L_{ev} = 0.11\%$ against the expected deviation of 0.25%. This is quite within the limits of experimentation and is much better than was found for the volume ratio; ($\Delta \ln = 0.25\%$ against 0.25%).[1] In the critical region the agreement is far better than could be expected, the difference being only 0.4% at 360°. On the other hand, near the melting point the discrepancy between calculated L_{ev} and that extrapolated by the Bureau of Standards is undoubtedly larger than any possible error of extrapolation, namely, 0.8–0.5% between 0 and 30°.

On the whole, taking into consideration that in the proposed equation there are only three constants and that it applies to an interval of about 300°, we can say that its accuracy is approaching that of the empirical equation of the Bureau of Standards with four constants ($\Delta L_{ev} = 0.11\%$ against 0.04%), the latter being designed only for the interval 0–270°.

Before proceeding any further we have to test equation (6) to see if it satisfies certain theoretical requirements. It has been shown by Gibbs on the basis of strict thermodynamical relations and with the aid of his model of the "primitive" surface that

TABLE I

WATER

Latent heat: $k = 17.678$; $m = 0.418097$; $n = 1.01292$

t, °C.	τ	$S = \frac{L_{ev}}{T}$ cal./mole. observed	Latent heat,[a] cal. per gram obsd.	Latent heat,[a] cal. per gram calcd.	Differences actual cal.	Differences ΔL_{ev}%
0	0.42196	(39.3568)	(596.467)	591.387	−5.080	0.8
+20	.45287	(36.0049)	(585.628)	582.761	−2.867	.5
40	.48376	(33.0654)	(574.517)	573.323	−1.194	.2
60*	.51467*	30.4615	563.083	563.083	0*	0*
80	.54557	28.1316	551.236	552.049	+0.813	.15
100	.57647	26.0265	538.874	540.100	+1.226	.22
120	.60738	24.1053	525.849	527.158	+1.310	.25
140	.63828	22.3338	511.992	513.138	+1.136	.20
160	.66918	20.6823	497.088	497.916	+0.828	.15
180	.70008	19.1257	480.903	481.312	+ .409	.08
200*	.73098*	17.6406	463.138	463.138	0*	0*
220	.76189	16.2062	443.468	443.120	− .348	.09
240	.79279	14.8017	421.463	420.941	− .522	.10
260	.82369	13.4064	396.611	396.086	− .525	.12
280	.85459	11.9956	368.189	367.830	− .359	.10
300	.88549	10.5370	335.115	335.019	− .096	.03
320	.91639	8.9773	295.474	295.613	+ .139	.04
340	.94730	7.2036	245.092	245.264	+ .172	.07
350*	.96275*	6.1541	212.799	212.799	0*	0*
360	.97820	4.8748	171.267	170.621	− .646	.40
374.11	1.00000	0	0	0	..	..

Average differences:		
40–350°	Proposed equation	0.11%
0–270°	Empirical equation of the Bur. Standards	.04%
Estimated accuracy of proposed equation		.25%

Proposed equation:

$$S_{ev} = \frac{L_{ev}}{T} = \frac{k'''(1 - \tau^2)^{m'''}}{\tau^{n'''}} \text{ cal./mole, range 40–350°}$$

Empirical equation Bureau of Standards:

$$L_{ev} = A(t^\circ_{cr} - t^\circ)^{2} - B(t^\circ_{cr} - t^\circ) + C(t^\circ_{cr} - t^\circ)^{0.5} - D(t^\circ_{cr} - t^\circ)^{0.25}$$

Range: 0–270°

* Asterisks mark reference points.

[a] Values in parentheses are extrapolated by the Bureau of Standards.

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(14) Latent heat and empirical equation (0–270°): N. S. Osborn, H. F. Stimson and E. F. Fiock, *Bur. Standards J. Research*, **5**, 411 and 478 (1930). Latent heat up to t° crit.: N. S. Osborn, H. F. Stimson and D. C. Ginnings, Preliminary Report, *Mech. Eng.*, **57**, 162 (1935).

(15) M. Jacob and W. Fritz, *Physik. Z.*, **20**, 651 (1935).

different properties will reach different limiting values at the critical point.[16] Thus for the latent heat and the latent heat gradient it follows, at the critical temperature

$$L_{ev} = T(S_{gas} - S_{liq}) = 0 \qquad (7)$$

$$dL/dT = S_g - S_l + T\left(\frac{dS_g}{dT} - \frac{dS_l}{dT}\right) = -\infty \qquad (8)$$

The two conditions are then that L_{ev} should approach the value zero and that the rate of its change with temperature should approach minus infinity as τ approaches unity.

It is obvious that the proposed equation (6) will satisfy the first requirements, since according to the theory of limits the term $(1-\tau^2)m'''$ should approach zero as a limit when $\tau = 1.000$ for cases where the exponent m is positive.[17]

In order to test the latent heat gradient we have to differentiate equation (6) with respect to T, thus obtaining

$$\frac{dL_{ev}}{dT} = \frac{-k'''(1 - \tau^2)^{m'''-1}[2m''' - n''' + 1 + (n''' - 1)/\tau^2]}{\tau^{n'''-2}} \text{ cal./degree} \qquad (9)$$

At the critical point the expression in the square brackets of eq. (9) reduces to $2m'''$, while the term $(1-\tau^2)^{m'''-1}$ becomes infinitely large. This again follows from the theory of infinite series,[17] namely: the expression $(1 - x)^{-a}$ approaches infinity as x approaches unity. Since for water $m''' = 0.418$, the exponent $m'''-1$ will be negative and the limit $-\infty$ will be reached at $\tau = 1.000$

$$\lim_{\tau \to 1.000} (1 - \tau^2)^{m'''-1} = -\infty \qquad (10)$$

The limiting value of the latent heat gradient now can be shown easily to approach $-\infty$. The limit of a product is equal to the product of the limits of the composing terms, whence

$$\left\{\frac{dL_{ev}}{dT}\right\}_{cr} = -2k'''m''' \lim_{\tau \to 1.000} (1 - \tau^2)^{m'''-1} = -\infty \qquad (11)$$

We thus see that at the critical point the latent heat gradient will become negatively infinite in accordance with the above requirement.

In view of the fact that the proposed equation (6) gives correct limiting values for the latent heat and its rate of change with temperature at the critical temperature and since the agreement is good in the long interval 40–350°, we feel that at least for water it is possible to express latent heat as a function of (reduced) temperature alone within the limits of observation.

The further testing of the equation is prevented by the lack of long range measurements on latent heat of other substances. The use of the Clapeyron–Clausius equation as a check on the proposed formula is not reliable because its accuracy depends largely on the accuracy of the term dp/dT and consequently on the equation of state used in each particular case. In some instances the error in dp/dT amounts to 3% and more at the end-points: the melting point and the critical region, as was shown for Biot's pressure formula and the latent heat of organic liquids by Mills.[18]

Before leaving the subject we might give a semi-theoretical proof of the proposed equation for latent heat. For perfect gases Kirchhoff's law states[19]

$$\frac{dL_{ev}}{dT} = C_{p\,gas} - C_{p\,liq} = -c = \text{constant} \qquad (12)$$

where C_p is the molar specific heat of gas and liquid, respectively, and is assumed independent of temperature for an ideal substance.

The expression (12) can be integrated between limits T and T_{cr}

$$\int_T^{T_{cr}} dL_{ev} = \int_T^{T_{cr}} (C_{p\,gas} - C_{p\,liq})\,dT = -c\int_T^{T_{cr}} dT \text{ where } c = \text{constant} \qquad (13)$$

$$L_{ev_{T_{cr}}} - L_{ev_T} = -c(T_{cr} - T) = -cT_{cr}(1 - \tau) \qquad (14)$$

changing all − signs for + and remembering that $L_{ev} = 0$ at T_{cr}, we get

$$L_{ev} = cT_{cr}(1 - \tau) \qquad (15)$$

Dividing both sides by T and simplifying we obtain for the entropy of evaporation

$$S_{ev} = \frac{L_{ev}}{T} = c\frac{(1 - \tau)}{\tau} \qquad (16)$$

where c is a constant. Equation (16) shows that for perfect vapors both the entropy of evaporation and the latent heat should be proportional to $(1 - \tau)/\tau$. In the case of real vapors the relationship is expected to be more complicated, since the factor c is not a constant—the difference in specific heats of the two phases is in itself a function of temperature.

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(16) W. Gibbs, "Scient. Papers," Vol. I, pp. 34–46 and 100–134. Also an easy and simple account is given in: J. R. Partington, "A Textbook of Thermodynamics," D. Van Nostrand Co., New York, N. Y., ed. 1913, pp. 240–252 and especially pp. 246 and 249.

(17) T. J. I'A Bromwich, "Theory of Infinite Series," Macmillan & Co., London, 1908, Ch. VIII, p. 152.

(18) J. E. Mills, *J. Phys. Chem.*, **8**, 383 and 394 (1904).

(19) A clear statement of Kirchhoff's law can be found in: K. Jellinek, "Lehrbuch der phys. Chem.," Vol. 1, Verlag von Ferdinand Enke, Stuttgart, 1928, pp. 97–98. W. Nernst, "Theoretical Chemistry," Macmillan & Co., London, 1911, p. 57.

The proposed equation (6)

$$S_{\text{ev}} = \frac{L_{\text{ev}}}{T} = k''' \frac{(1-\tau^2)^{m'''}}{\tau^{n'''}} \qquad (6)$$

is very similar to the above expression (16) except that it contains exponents. The exact thermodynamical derivation of this equation cannot be given as long as the specific heats of liquid and vapor are not yet known as functions of temperature.

The next property to be considered is the vapor volume. *A priori* the reduced volume $V_{\text{gas}}/V_{\text{cr}}$ may be thought analogous to the term $V_{\text{gas}}/V_{\text{liq}}$ which is the relative volume during the change of state of aggregation. In the two ratios the numerators are the same and the denominators differ in that the variable V_{liq} is replaced by a constant V_{cr}. The two corresponding curves ln $V_{\text{g}}/V_{\text{cr}}$ and ln $V_{\text{g}}/V_{\text{liq}}$ in Fig. 1 quite support this view: they are neighbors in the coördinate system and they have very similar shapes.

One is tempted again to apply the original equation (1)

$$\ln \frac{V_{\text{gas}}}{V_{\text{cr}}} = k'' \frac{(1-\tau^2)^{m''}}{\tau^{n''}} \qquad (17)$$

and

$$V_{\text{gas}} = V_{\text{cr}}\, e^{k''\frac{(1-\tau^2)^{m''}}{\tau^{n''}}} \text{ cm.}^3/\text{g.} \qquad (18)$$

The equation (18) was tested against the vapor volume data for water calculated from an exact equation of state and published last year by the Massachusetts Institute of Technology (0–340°) and the Bureau of Standards data (0–370°), calculated from observed latent heat and the Clapeyron–Clausius equation. The two sets of data agree within 0.03% on the average, except in the critical region where the latter set seems the more reliable (340–370°). The critical volume at 374.11° is that extrapolated by Keyes.[20]

In Table II we give the results of our calculations on volume. In column 3 are given the ln $V_{\text{g}}/V_{\text{cr}}$ values derived from the M. I. T. data (0.–340°) and from the Bureau of Standards data (350–370°). In column 4 are shown the differences between these and the ln values calculated from proposed equation (17). At the bottom of this column are given the average percentage deviation and the estimated accuracy of equation (17).

The expected accuracy of equation (17) is the same as that of equation (1) for the volume ratio. The error in the critical temperature is the same—0.15%. The error in vapor volume is small for water and has a negligible effect on the ln $V_{\text{g}}/V_{\text{cr}}$. The error in critical volume is also not large. The last two may be considered as amounting to less than 0.1% and the total error will be 0.25% as before.[1] The average deviation actually found is only $\Delta \ln = 0.09\%$ for the whole range; this is much better than could be expected, particularly in the critical region where $\Delta \ln = 0.5\%$ at 360°.

In the following two columns are given the volumes themselves in cc. per gram calculated from the proposed equation (18) and compared with the corresponding data. In the last column is given the percentage deviation ΔV for each temperature as well as the average $\Delta V\%$ for the intervals 20–374.11°. For comparison are also shown the average tolerance of the Clapeyron–Clausius equation and the average difference between it and the Keyes equation of state. All three equations are shown at the bottom of Table II.

When we come to volumes themselves it may appear at first glance that equation (17) would not hold at very high temperatures due to large deviation in the ln $V_{\text{g}}/V_{\text{cr}}$. Here, however, the effect is diminished rather than increased, for the following reason. In calculating the volumes we are dealing not with the log but with the function itself. At high temperatures (about 340°) the natural log of the reduced volumes approaches unity and for these small values of the log a large percentage difference in its value corresponds to a very small percentage difference in its number. Therefore, a 1% deviation in the log corresponds to only a fraction of a per cent. in the volume itself. We see that equation (18) is applicable at the very highest temperatures. In examining the last column of Table II we actually see that at 360° the calculated V_{gas} differs by only 0.5% from the Bureau of Standards value. In the interval 20–350°, the agreement also is very good, the average difference being only 0.17%, which compares well with the tolerance of Clapeyron–Clausius equation —0.13% (0.1% due to L_{ev} measurements and 0.03% due to the term $\mathrm{d}p/\mathrm{d}T$). On the contrary near the melting point our calculations are decidedly off, the discrepancy amounting to 2–0.5% between 0 and 30°. Of course, this is to be expected in this interval, because for large values of the natural log the error in the numbers $\Delta V\%$ is correspondingly large.

We see that the reduced volume equation (18)

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(20) Saturation vapor volumes: F. G. Keyes, L. B. Smith and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **70**, 319 (1936); and N. S. Osborn, H. F. Stimson and E. F. Fiock, *Mech. Eng.*, **57**, 162 (1935); critical volume: L. B. Smith and F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934).

TABLE II

WATER

Vapor volumes: $k = 3.2813$; $m = 0.47169$; $n = 1.5190$

t,°C.	τ	$\ln V_g/V_1$ Keyes equation	Δ ln, % proposed	Volumes cc./g. I Keyes equation	II Proposed	ΔV, % I–II
0	0.42196	11.0753	+0.2	206300	210361	2.0
+20	.45287	9.80362	+ .05	57824	58162.3	0.5
40	.48376	8.71836	+ .01	19543	19568.2	.15
60*	.51467	7.78385	0*	7678.3	7678.3	0*
80	.54557	6.97192	+ .01	3409.2	3412.4	.07
100	.57647	6.26018	+ .02	1673.2	1675.55	.13
120	.60738	5.63086	+ .025	891.65	892.972	.15
140	.63828	5.06931	+ .02	508.53	509.208	.12
160	.66918	4.56376	+ .02	306.76	307.020	.09
180	.70008	4.10446	+ .01	193.80	193.860	.03
200*	.73098	3.68308	0*	127.18	127.180	0*
220	.76189	3.29267	− .01	86.070	86.036	.04
240	.79279	2.92653	+ .01	59.684	59.682	.01
260	.82369	2.57875	+ .04	42.149	42.184	.10
280	.85459	2.24295	+ .10	30.122	30.188	.20
300	.88549	1.91190	+ .20	21.625	21.709	.45
320	.91639	1.57550	+ .25	15.438	15.517	.50
340	.94730	1.21495	+ .20	10.764	10.801	.35
350*	.96275	1.01215	0*	8.798	8.798	0*
360	.97820	0.77508	+ .60	6.941	6.907	.50
374.11	1.00000	0	....	3.1975	3.1975	.00
		Average Δ ln =	.09		Average differences	
		Estimated accuracy =	.25	Proposed—Keyes eq. 20–360°		.17
				Clapeyron–Keyes 20–340°		.03
				Accuracy of Clapeyron eq.		.13

Proposed equation: range 20–360°: $\ln V_g/V_{cr} = k'' \dfrac{(1-\tau^2)^{m''}}{\tau^{n''}}$

Empirical equation: Keyes, Smith and Gerry, range 0–340°: $V_{g\,sat} = \dfrac{AT_s}{P_s} + B_0 - B_s$

where $B_0 = C - (D/T)10^{f/T^2}$

$B_s = 1/(a + bx^{1/8} + cx)(1 + dx^{10})$

$T_s = t_s + 273.16$ and $x = t_{cr} - t_s$

Clapeyron–Clausius equation: $V_g - V_1 = \dfrac{L_{ev}}{T(\mathrm{d}p/\mathrm{d}T)}$

applies well for water in the long interval of about 300° and on the whole compares favorably with the Clapeyron–Clausius equation. It is to be noticed in this connection that the Keyes equation of state agrees with Clapeyron–Clausius far more closely (0.03%) (see Table II).

To test the volume formula for the limiting values we have again calculated the volume gradient and the vapor volume at the critical point. It is obvious from equations (17) and (18) that $\ln V_g/V_{cr}$ will be equal to zero and the reduced vapor volume will be unity at the critical point, thus satisfying the physical conditions and Gibbs' postulates.[16] The volume gradient $\mathrm{d}V/\mathrm{d}T$ is derived easily from equation (18) in a manner similar to that for latent heat gradient, giving

$$\mathrm{d}V/\mathrm{d}T = \frac{-V_{gas}\cdot k''(1-\tau^2)^{m''-1}}{T_{cr}\cdot \tau^{n''-1}} (2m'' - n'' + n''/\tau^2) \text{ cc./ degree} \qquad (19)$$

At the critical point the expression for $\mathrm{d}V/\mathrm{d}T$ will again become infinite, because the exponent $m'' = 0.47$ and $m''-1$ is negative. This will make the term $(1-\tau^2)^{m''-1}$ approach infinity as τ approaches unity as was shown above for $\mathrm{d}L_{ev}/\mathrm{d}T$. The limit for $\mathrm{d}V/\mathrm{d}T$ at the critical temperature will be

$$\frac{\mathrm{d}V}{\mathrm{d}T_{cr}} = \frac{-V_{cr}}{T_{crit}} \frac{2k''m''}{1} \lim(1-\tau^2)^{m''-1} = -\infty \qquad (20)$$

In other words, according to the proposed equation (18) the vapor volume will approach its critical value with a negative infinite rate at the critical point. This agrees exactly with the theoretical requirements which follow from Gibbs' thermodynamic surface,[16,21] namely

$$\left.\begin{array}{r}\text{In the vicinity of } T_{cr} \;\; \mathrm{d}T/\mathrm{d}v > 0 \\ \text{at } T_{cr} \;\; \mathrm{d}T/\mathrm{d}v = 0\end{array}\right\} \qquad (21)$$

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(21) See J. R. Partington, "A Textbook of Thermodynamics," D. Van Nostrand Co., New York, 1913, p. 240 and especially p. 248.

The fact that the limiting conditions eq. (21) are satisfied and the general agreement with reliable volume data is good leads to the conclusion that for water the vapor volume also can be expressed in terms of reduced temperature with required accuracy.

We now come to the last of the properties discussed here, the vapor pressure. The equation of Cederberg (4) cited in the beginning of this article suggests that the natural logarithm of the reduced pressure is an exponential function of reduced temperature. The defects of his equation, however, show that this function must be of a different form from that devised by Cederberg.

Such a new relation is again suggested to us by Fig. 1 of the present paper. In examining the lowest curve, ln P_{cr}/P_{satd} we see its similarity to the others, except in the region 0.8–1.0 of the critical temperature. One should expect then some slight modification of equation (1) to hold for this magnitude as well as for the rest.

In accordance with these conclusions we first tried a general form of equation (1) containing 4 constants

$$\ln P_{cr}/P_s = k' \frac{(1+\tau)^{s'}(1-\tau)^{m'}}{\tau^{n'}} \qquad (22)$$

Tested on water it gave an average deviation of 0.5% which we consider insufficiently accurate.

We returned to the original form (1) with 3 constants

$$\ln P_{cr}/P_s = k' \frac{(1-\tau^2)^{m'}}{\tau^{n'}} \qquad (23)$$

and

$$P_{satd} = P_{cr}\, e^{-k' \frac{(1-\tau^2)^{m'}}{\tau^{n'}}} \text{ atm.} \qquad (24)$$

where k', m', n' are parameters different from those previously given.

This equation was checked against the latest data on vapor pressure of water. The values between 0–100° are based on the observations of the Reichsanstalt in 1910 and adjusted by the empirical equation of the Bureau of Standards. The values between 100 and 374.11° are measurements of the Massachusetts Institute of Technology, while the critical pressure is an extrapolation from the above data by Keyes.[22]

In Table III we give as before the complete calculations. The columns follow in the same order as in Table II: the observed ln P_{cr}/P_s; the deviations, per cent. $\ln_{obsd} - \ln_{calcd}$, including their average, compared with the estimated accuracy of the proposed equation; the observed and calculated pressures in atmospheres and the percentage differences $P_{obsd} - P_{calcd}$ including the average differences $\Delta P\%$. As before we give the average accuracy of the Bureau's equation. Finally we show the actual form of the Bureau's equation together with that of the proposed equation (23).

In order to have a complete check on the formula we have calculated the pressure gradient for the whole range including the critical point and compared these values with the pressure gradient derived from the Bureau of Standards equation. The actual values dP/dT derived from the two formulas together with the corresponding differences in percentages are given at the bottom of Table III.

The estimated accuracy of the pressure equations (23, 24) was found to be exactly the same as for latent heat and vapor volume. This follows from the fact that (as before) the error in T_{cr} is 0.15%, the error in observed vapor pressure is very small for water and can be neglected, while the error in the critical pressure will influence the ln P_{cr}/P_s to not more than 0.1%, giving again the total estimated accuracy equal to 0.25%.

The average deviation actually found is 0.12% between 20 and 350°, which is again entirely within the limits.

In regard to the pressures themselves the same must be told as in respect to vapor volumes, namely, that the equation will give good results up to the critical temperature, since the deviation of the number is much smaller than the corresponding deviation of its natural log when the latter approaches the value unity. In examining the last column we find accordingly that the deviation is only 0.1% for pressure at 360°. The average difference is of the same order: ΔP = 0.08% between 60° and critical temperature, which compares fairly well with the average deviation of 0.02% shown by the Bureau's equation (7 constants) between 0° and T_{cr}. At the very low temperatures, 0–50°, we again find large percentage differences (4–2%) which, however, in terms of atmospheres are of small magnitude only.

It remains now to verify the limiting values for pressure and pressure gradient at the critical point as well as the whole range of dP/dT values derived from the expression (24).

It is obvious here (see eqs. 23–24) that at the critical point ln π and π will be equal to zero and

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(22) Pressures (0–100°): N. S. Osborn and C. H. Meyers, *Bur. Standards J. Research*, **13**, 1 (1934). Pressures (100–374°) and P_{cr}: L. B. Smith, F. G. Keyes and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137 and 139 (1934).

TABLE III

WATER

Vapor pressures: $k = 3.4771$; $m = 0.97084$; $n = 1.5058$

t, °C.	τ	ln P_{cr}/P_s obsd.	Δ ln % obsd. − calcd.	Pressures, atm. obsd.	Pressures, atm. calcd.	ΔP % obsd. − calcd.
0	0.42196	10.4967	+0.4	0.0060273	0.0057777	4.0
+20	.45287	9.1557	+ .2	.0230420	.0226646	1.6
40	.48376	8.0060	+ .06	.0727480	.0723783	0.5
60*	.51467	7.0120	0*	.196560	.196560	0*
80	.54557	6.1458	− .02	.467396	.467877	.10
100	.57647	5.3853	− .02	1.0000	1.00105	.10
120	.60738	4.7126	− .01	1.9595	1.96070	.06
140	.63828	4.1136	.00	3.5669	3.56696	.00
160	.66918	3.5764	.00	6.1032	6.10288	.00
180	.70008	3.0931	.00	9.8959	9.89576	.00
200*	.73098	2.6540	0*	15.3520	15.3520	0*
220	.76189	2.2542	.00	22.8970	22.8980	.00
240	.79279	1.8874	− .09	33.0440	33.0927	.15
260	.82369	1.5496	− .15	46.3220	46.4167	.20
280	.85459	1.2367	− .20	63.3430	63.4980	.25
300	.88549	0.9452	− .25	84.7760	84.9828	.25
320	.91639	.6721	− .25	111.402	111.609	.20
340	.94730	.4145	− .20	144.139	144.250	.08
350*	.96275	.2905	0*	163.164	163.164	0*
360	.97820	.1689	+ .60	184.260	184.079	.09
374.11	1.00000	0	...	218.167	218.167	.00

Average Δ ln = .12%

Estimated accuracy of proposed equation .25%

* Asterisks mark reference points.

Average differences:

Proposed eq. 60–374° .08

Bur. Standards eq. 0–374° .02

Proposed equation: $\ln P_{cr}/P_s = k' \dfrac{(1-\tau^2)^{m'}}{\tau^{n'}}$

Bur. Standards eq.: $\log_{10} P = A + B/T + (Cx/T)(10^{Dx^2} - 1) + E(10^{Fy^{5/4}})$
where: $x = T^2 - K$, $y = t^{\circ}_{cr} - t^{\circ}$ and A, B; C, D, E, F and K are constants.

Pressure gradient dp/dT of water

t, °C.	dp/dT calculated Bur. Stan. Eq.	dp/dT calculated Proposed eq.	Diff., %
0	0.00043729	0.000429495	+2.0
+20	.00142704	.00142322	−0.3
40	.00387960	.00388702	+ .2
60	.0091004	.00912506	+ .2
80	.0189322	.0189593	+ .15
100	.035699	.0357119	+ .04
120	.062076	.0620613	− .02
140	.100934	.100891	− .04
160	.155201	.155232	+ .02
180	.227701	.227793	+ .04
200	.321129	.320556	− .15
240	.580950	.582725	+ .3
260	.75246	.754938	+ .3
280	0.95570	0.958399	+0.3
300	1.19479	1.19628	+ .09
320	1.47572	1.47339	− .15
340	1.80896	1.79913	− .6
350	2.00197	1.98695	− .8
360	2.22115	2.16762	−2.5
370	2.48495	2.413	−3.0
373.5*	2.607 (interp.)	2.666	+2.5
374.0	2.63079	2.878	+9.0
374.05	(Not given)	2.9295	
374.11	(Not given)	∞	....

Average diff.: (20–320°) 0.13

Accuracy Bur. Stand. (0–374°) .03

unity, respectively, which are the values required by theory.

As to the pressure gradient it will be exactly the same in form as the volume gradient but with the sign reversed

$$\mathrm{d}P/\mathrm{d}T = \frac{P_s}{T_{cr}} k' \frac{(1-\tau^2)^{m'-1}}{\tau^{n'-1}} (2m' - n' + n'/\tau^2) \quad (25)$$

At the critical temperature this will reduce to

$$(\mathrm{d}P/\mathrm{d}T)_{cr} = \frac{P_{cr}}{T_{cr}} 2k'm' \lim (1-\tau^2)^{m'-1} = +\infty \quad (26)$$

because $m' = 0.97$ and m'^{-1} is a small negative fraction. This shows that the vapor pressure derived from proposed equation (24) will approach its critical value at a positive infinite rate. This is contrary to general conceptions, since it was shown by Planck that dP/dT should reach a finite value at the critical temperature.[23] This follows from the theoretical deduction that the first derivative dP/dT and the partial derivative at con-

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(23) M. Planck, *Ann. Physik*, [3] **15**, 457 (1882).

stant volume $\left\{\frac{\delta P}{\delta T}\right\}_{v = c}$ approach each other at high temperatures and finally must become equal at the critical point; the partial derivative must of course be finite at any temperature, hence

$$\lim_{T \longrightarrow T_{cr}} \left(\frac{dP}{dT}\right) = \left(\frac{\delta P}{\delta T}\right)_{v = c} = \text{finite number} \qquad (27)$$

In order to investigate more fully the discrepancy for dP/dT "proposed," we have extended the calculations up to the highest values of τ, namely, up to $\tau = 0.9999$. This gave us an idea of the rate at which dP/dT approaches infinity. Actual figures in Table III show that even at $\tau = 0.9999$ (374.05°) the value dP/dT is still a small number only 10% higher than the value given by the Bureau of Standards at 374.0°, namely, 2.9295 atm./deg. against 2.6308 atm./deg.

We come to the conclusion that at a temperature only 0.05° lower than the critical the pressure gradient derived from the proposed equation is finite and quite close to the value derived from a very accurate pressure equation of an entirely different type. It is only in the infinitesimal interval of 0.05°, which is entirely outside of the experimental limits for T_{cr}, that dP/dT would acquire infinite value.

Since the critical temperature of water is uncertain by ±0.05° and since for other substances the precision is still less, we feel that the limit for the pressure gradient $(dP/dT)_{cr}$ may be taken as equal to dP/dT at $0.9999T_{cr}$ and, consequently, finite.

At temperatures other than the critical the dP/dT "proposed" can be considered in fairly good agreement with the latest data. The Bureau of Standards equation yields dP/dT values which are in perfect agreement with the values of Keyes, Smith and Gerry, the difference being 0.03% on the average. From Table III it is evident that the deviation of the proposed equation from that of the Bureau of Standards averages 0.13% between 20 and 320°. This is notably close agreement in view of the small number of constants in equation (23) as compared with the other two formulas. On the other hand, at 0 and at 350° the proposed equation deviates considerably from the reliable data, since there the discrepancy amounts to 2% and increases up to 9% at 374.05°. The signs of the deviations are rather normally distributed, but above 370° (equation 25) yields values which are always too high.

If we combine the above results with respect to the pressure equation we can say that the pressure itself gives a very small deviation and the same is true for the pressure gradient for an interval of about 300°. Also the limiting values of P_s and dp/dT are given correctly at the critical point defined within ±0.05°. Consequently the vapor pressure of water and its derivative can be expressed as functions of reduced temperature alone within experimental limits.

The form of the function here chosen seems superior to that of Cederberg in several points: (1) It has the same number of constants and for their evaluation no previous knowledge of pressure data is required except for three isolated values. (2) The critical pressure has little effect on its accuracy and no arbitrary adjustment of this or other data is necessary. (3) It is influenced much less by errors in critical temperature, since the reduced temperature, or any other variable does not enter in the exponents m' and n'. Therefore it is expected to give better results for substances with low critical temperature.

For water its agreement with experiment is of the same order as Cederberg's calculations ΔP = 0.08% (proposed) against 0.1% and Δdp/dT is 0.13% (20–320°) (proposed) against 0.2% (100–180°).[24]

We express our thanks to Dr. Henry Fleishmann and the Educational Alliance, New York, for renewed financial assistance given to one of us (C. S.) during this work.

Conclusions

We now can summarize our findings with respect to the investigated thermal magnitudes. We see that the first prediction of Dieterici quoted on p. 784 of this article is verified completely.

1. The study of the volume ratio as a function of reduced temperature leads to the formulation of a relationship between latent heat and (reduced) temperature alone, which holds within experimental limits.

2. It further leads to a functional relationship between pressure and volume and (reduced) temperature alone which likewise holds with required accuracy.

The method of approach in the present work was, however, different from that of Dieterici. Instead of a lengthy path of term by term sub-

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[24] The derivative of Cederberg's equation was not tested at very low or very high temperatures.

stitution suggested by him, the desired functions were obtained from analytical relations between the respective curves.

The similarity in the shapes of the graphs $\ln P_{cr}/P_s$; $\ln V_g/V_{cr}$; $\ln V_g/V_l$ and L_{ev}/T as functions of τ suggested that all these curves belong to one and the same family of algebraic functions and can be expressed by a common equation

$$y = k\,((1 - \tau^2)^m/\tau^n)$$

differing only in the values of the parameters k, m and n.

The close interrelation between all these properties is further evident from the fact that the values of the above parameters are close to each other when different properties of one and the same substance are compared, as the following table shows for water.

Property	k	m	n	Substance
Latent heat	17.678	0.41810	1.0129	H_2O
Volume ratio	4.122	.3770	1.338	
Vapor volume	3.281	.47169	1.5190	
Vapor pressure	3.4771	.97084	1.5058	

We have tested here only one substance, water, yet the good results obtained with this substance, having an extremely long saturation line, give every reason to believe that other substances will give support to the above findings.

It remains to see whether the second prediction of Dieterici is correct, namely, that a detailed investigation of reduced properties will lead to the reëstablishment of the principle of corresponding states at least for organic liquids and that the deviations, where encountered, will be found as due to differences in the critical data. This we expect to do in Part II of this study.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Thermodynamic Properties of Substances as a Function of Reduced Temperature. II. Vapor Pressures of Liquids and the Principle of Corresponding States

BY HAROLD A. FALES AND CLARA S. SHAPIRO

In the first part of the present article we calculate the latent heat, the vapor volume and the vapor pressure of water using the equations

$$L_{ev}/T = k''' \frac{(1 - \tau^2)^{m'''}}{\tau^{n'''}} \qquad \text{(Ia)}$$

$$\ln V_g/V_{cr} = k'' \frac{(1 - \tau^2)^{m''}}{\tau^{n''}} \qquad \text{(Ib)}$$

$$\ln P_{cr}/P_s = k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}} \qquad \text{(Ic)}$$

which are all of the same type but differ in the values of the parameters k, m and n.

In this second part of the paper we will apply the equation of reduced pressure to a large number of substances with a view to arriving at some modification of the principle of corresponding states which might embrace different types of compounds.

The thirty substances selected for the test are the same as chosen previously in the study of orthobaric densities[1] with one exception: carbon dioxide is substituted for sulfur dioxide in view of its greater importance and because its vapor pressure and pressure gradient have been determined recently with great precision by the Bureau of Standards.[2] The calculations for carbon dioxide (entire range of saturation) are shown here in detail in Table I which gives: the observed $\ln P_{cr}/P_s$; the percentage differences between observed and calculated ln values; and the average percentage deviation. The estimated accuracy of the equation for carbon dioxide also is given at the bottom of column 4. In examining the figures we see that the agreement is very good throughout, since the actual average deviation ($\Delta \ln = 0.04\%$) is far smaller than the estimated one ($\Delta \ln = 0.25\%$).

In the last three columns we give the observed and calculated pressures and the percentage differences $\Delta P\%$ including the average percentage difference. This is compared with the average deviation of the empirical equation of the Bureau of Standards.[2]

We see that the pressures themselves are represented with high precision up to the very highest temperatures. In the critical region at 31.0° the difference is only 0.1% and the average deviation for the whole temperature range is only 0.09%.

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(1) H. A. Fales and C. S. Shapiro, THIS JOURNAL, **58**, 2418 (1936).

(2) C. H. Meyers and M. S. Van Dusen, *J. Research Bur. Standards*, **10**, 381 (1933).