

## GENERAL LAW FOR VAPOR PRESSURES. PART II.

BY SANFORD A. MOSS.

IN the preceding article<sup>1</sup> was deduced a general law connecting saturation temperatures and vapor pressures for all substances, on the basis of a relation given by Ramsay and Young. The law connects the absolute saturation temperatures  $T_a$  and  $T_b$  of two substances, corresponding to the same vapor pressure, by the symmetrical relation

$$\frac{1}{T_b} = c \frac{1}{T_a} + k \quad (1)$$

$c$  and  $k$  are constants for each pair of substances, for all vapor pressures. Either substance may be a vaporizing liquid or a subliming (volatilizing) solid. The two temperatures might also refer to the solid and liquid phases of the same substance.

Forms equivalent to (1) have also been derived from Ramsay and Young's relation by Ayrton and Perry<sup>2</sup> and J. D. Everett.<sup>3</sup>

As in the case of the original relation given by Ramsay and Young, we may determine by the law (1) the entire vapor pressure curve for a substance from two observations and the known curve of some standard substance.

In the preceding article the form (1) was supposed to be equivalent to the relation given by Ramsay and Young. However, it turns out that there are two quite different forms in which the statement of Ramsay and Young may be expressed mathematically. One form leads to the symmetrical law (1) and the other to a quite different non-symmetrical form. The latter form seems to be the one preferred by the authors of the original relation.

The purpose of this paper is to go into details in this matter, and

<sup>1</sup> PHYSICAL REVIEW, Vol. 16, 1903, p. 356.

<sup>2</sup> Phil. Mag., Vol. 21 (series 5), 1886, p. 259.

<sup>3</sup> Phil. Mag., Vol. 4 (series 6), 1902, p. 335.

to show that the symmetrical law (1) is to be preferred over the other form for many reasons, and that it is very nearly, if not exactly, a law of nature. A number of related points discussed in various isolated papers will also be brought together systematically.

TEMPERATURE RATIO LAWS AND COMPARISON WITH  
OBSERVATIONS.

A relation exactly equivalent to (1) is

$$T_a/T_b = kT_a + c. \quad (2)$$

Hence we have the following as a consequence of the symmetrical law (1). If values of  $T_a/T_b$ , the ratio of absolute saturation temperatures at same vapor pressure for two substances, be found for various vapor pressures, and plotted against  $T_a$ , the *numerator* of the ratio, the points will lie on a straight line.

The fact that saturation temperature observations satisfied a law similar to the one just stated, was the particular point originally brought out by Ramsay and Young. At times they used the identical law above given, and at times another form, as will be discussed presently.

In this work, Ramsay and Young found that the constant  $k$  was always small so that the term  $kT_a$  is comparatively small as compared with  $c$ . Hence  $T_a/T_b$  is nearly but not quite constant. For the case of pairs of substances from a homologous series, such as the various ethers,  $k$  is zero, and the ratio  $T_a/T_b$  is exactly constant.<sup>1</sup>

Now Ramsay and Young in some cases and Travers in all cases plot the absolute temperature ratio of (2) not against the *numerator*, but against the *denominator*. That is, they use the reciprocal of the left hand member of (2), corresponding to the dissimilar and non-symmetrical form

$$T_b/T_a = k'T_a + c'. \quad (3)$$

Evidently, if values of  $T_a/T_b$  give a straight line when plotted against values of  $T_a$ , so that (2) is satisfied, then values of the reciprocal,  $T_b/T_a$ , will not give a straight line but a curve. It will probably always be very flat, however, but nevertheless such that (3) is

<sup>1</sup>Phil. Mag., Vol. 20, series 5, 1885, p. 530; Vol. 21, series 5, 1886, p. 33; Vol. 22, series 5, 1886, p. 37. Here the constant above called  $k$  is called  $c$ .

not exactly satisfied. If the values used are from observations and are slightly irregular, and if the range covered is not very great, the points may seem to follow a linear law, and may apparently satisfy the non-symmetrical form (3). It will be shown however that the points from various published observations fall in a straight line at least as well and often better, if the symmetrical form (2) is used rather than the non-symmetrical form (3) and also that it is more rational to use the symmetrical form.

In the original paper on the subject, by Ramsay and Young,<sup>1</sup> the law is given as being that the ratio of absolute saturation temperatures is a linear function of one of them. There is no statement as to which one, numerator or denominator. In the paper are given tables for the cases of ethyl alcohol,  $C_2H_6O$ , methyl alcohol,  $CH_4O$ , ethyl oxid,  $C_4H_{10}O$ , ethyl bromide,  $C_2H_5Br$ , ethyl chloride,  $C_2H_5Cl$ , ethylene,  $C_2H_4$ , oxygen,  $O_2$  (3 comparisons), and mercury, Hg, obtained by plotting actual vapor pressure observations according to the symmetrical form (2). That is, saturation temperature ratios are plotted against numerators. The law is shown to be verified as the observations lie very nearly on a straight line.

On the contrary, the opposite and non-symmetrical form (3) is used for a number of other substances and temperature ratio is plotted against denominator. No note is made regarding the change in procedure. Aryton and Perry have made some remarks on this paper<sup>2</sup> and also seem to have noted the two different forms used. As already stated they deduce a form equivalent to (1) which they also regard as preferable on account of symmetry.

For the case of carbon bisulphid,  $CS_2$ , one of the substances for which Ramsay and Young use the non-symmetrical form, the writer has replotted the given figures in the symmetrical form. The resulting points lie equally well on a straight line. A similar situation doubtless exists with the other cases where the non-symmetrical form was used, and the symmetrical form would undoubtedly have given at least as good results.

The paper gives as an algebraic expression of the law

$$R' = R + k(T' - T).$$

<sup>1</sup> Phil. Mag., Vol. 21, series 5, 1886, p. 33.

<sup>2</sup> Phil. Mag., Vol. 21, series 5, 1886, p. 259.

(The constant  $k$  is called  $c$  in the paper.)  $R$  and  $R'$  are ratios of absolute saturation temperatures of two substances at same vapor pressure, for two different vapor pressures.  $T$  and  $T'$  are temperatures of one of the substances. No statement is made as to which one, that of the numerator or denominator of the ratios. It is readily seen that this expression is equivalent to (2) or to (3) according as one or the other is used.

A similar expression is given by Ramsay and Travers in the classic paper, "Argon and its Companions,"<sup>1</sup> and is repeated on page 236 of Travers' "Study of Gases." This is printed in both places.

$$\frac{T_a}{T_b} = \frac{T'_a}{T'_b} + k(T_a - T'_a).$$

However, the writer has been informed by Professor Travers that this is a mistake and that the last parenthesis should have been  $(T_b - T'_b)$ , as is also indicated by the context. This correction calls for plotting of temperature ratio against denominator, contrary to the symmetrical form (2). In the paper on argon, and in "Study of Gases," examples are given of the application of the law and temperature ratios are always plotted against denominator. This may therefore be considered as the form of law preferred by Ramsay and Travers.

The preceding paper was based on the statement of the law given immediately above and the symmetrical form (2) deduced therefrom. The fact that the formula was not printed as the authors intended was not known to the writer at the time. The whole of the preceding paper goes to show that the symmetrical form (2) is correct, regardless of the fact that it was deduced from a misprint; and additional evidence is given in this paper.

In the paper, "Argon and its Companions," observed values of vapor pressure of krypton, argon and xenon are given, agreeing fairly well with the form (3). The writer has replotted these observations, using instead the form (2), and has found much better agreement. For the case of krypton two observations are not included in the range of the chart given by Ramsay and Travers, and these do not

<sup>1</sup> Phil. Trans., Vol. 197 A, 1901, p. 68.

lie on an extension of the line through the other points. However, when reciprocals of the ratio are used, corresponding to the form (2), these points, as well as all of the others, fall almost exactly on a straight line. In the case of argon, the form (2) fits slightly better than the other form, while in the case of xenon there is no material difference, owing to observational irregularities. Ramsay and Travers give tables of vapor pressures of argon, krypton and xenon, smoothed by the use of the form (3). Evidently the use of (2), the form preferred by the writer, would give slightly different tables.

The form (2) has been applied by the writer to Miller's observations of vapor pressure of SO<sub>2</sub><sup>1</sup>, and found to agree very well for moderate temperatures, but to give some discrepancy at high values. The relation between T<sub>s</sub>, the saturation temperature of SO<sub>2</sub>, and T<sub>w</sub>, that of water vapor for the same pressure, is found to be

$$\frac{1}{T_s} = 1.6667 \frac{1}{T_w} - 0.00036.$$

In the preceding paper was given a table, reproduced herewith with some additions, for vapor pressures of water as computed from Ramsay and Young's observations on methyl alcohol by means of the law,

$$\frac{1}{T_w} = .9198 \frac{1}{T_a} - 0.0000307.$$

TABLE OF HIGH SATURATION TEMPERATURES OF WATER VAPOR.

Vapor Pressure. mm. Hg.	Saturation Temperatures, Degrees Centigrade.		
	From Methyl Alc. Obs.	From Cailletet's Obs.	From Formula "K."
45,000	275.9	274.8	276.0
50,000	282.9	281.5	283.0
55,000	289.3	288.0	289.5
60,000	295.2	294.0	295.6

Since the original table was published, observations by Cailletet have come to the attention of the writer, and interpolations from them are given in the table. They are very close to the computed figures, although slightly lower. It may be remarked however, that for lower pressures, Cailletet's temperature observations are slightly lower than those of both Regnault and Ramsay and Young,

<sup>1</sup> Trans. Amer. Soc. Mech. Engrs., Vol. 25, 1904, p. 182.

suggesting that all of his values may be slightly low. If so, the computed values are evidently almost exactly correct. The last column of the table will be referred to later.

INVESTIGATION OF RATIONALITY OF THE TEMPERATURE  
RATIO LAWS.

The law expressed by (1) is obviously mutual and  $1/T_a$  and  $1/T_b$  are each linear functions of the other. Similarly we may reverse (2) by writing it,

$$\frac{T_b}{T_a} = \left(-\frac{k}{c}\right) T_b + \frac{1}{c}.$$

Hence if we plot the reciprocal of the ratio on the left of (2) against the new numerator, we also have a linear relation. Hence if we use the form (2) it is immaterial as to which of a pair of substances is used as numerator or denominator. In other words the symmetrical form of the temperature ratio law is rational in so far that it is perfectly reversible.

The non-symmetrical form (3) does not turn out thus however. We may write it

$$\frac{T_a}{T_b} = \left(-\frac{k'}{c'}\right) \frac{T_a^2}{T_b} + \frac{1}{c'}.$$

Hence if  $T_b/T_a$  is a linear function of the denominator,  $T_a/T_b$  is not a linear function of the new denominator.

Hence if the form (3) is used for a given pair of substances, different results are obtained according to the one used as denominator and if the law holds in one form, the ratio cannot be inverted.

Another evidence of the rationality of the forms (1) and (2) is the fact that if the law holds for pairs consisting of two substances each compared with a third standard substance, it will necessarily hold for the pair consisting of the two different substances from the original pairs. Suppose for instance that the law holds for substances  $a$  and  $b$  and also for substances  $a$  and  $d$ . Then

$$\frac{1}{T_b} = c \frac{1}{T_a} + k,$$

$$\frac{1}{T_d} = c' \frac{1}{T_a} + k'.$$

All of the temperatures correspond to the same vapor pressure. By eliminating  $1/T_a$  from the two equations we obtain

$$\frac{1}{T_b} = \left(\frac{c}{c'}\right) \frac{1}{T_a} + \left(k - k' \frac{c}{c'}\right).$$

Thus the linear relation holds for the pair of substances  $b$  and  $d$ .

On the contrary this does not occur with the form (3), and if two pairs of substances satisfy it, there is not satisfaction after interchange. Using the form (3) in the above case

$$\frac{T_a}{T_b} = kT_b + c.$$

$$\frac{T_a}{T_d} = k'T_d + c'.$$

Eliminating  $T_a$  by division,

$$\frac{T_d}{T_b} = \frac{kT_b + c}{k'T_d + c'}.$$

Hence the ratio  $T_a/T_b$  is not linear in the denominator  $T_b$  so that the law is not satisfied.

As already shown, the original relations of the case just investigated are not exactly reversible. Hence by using other arrangements of subscripts in them, we can obtain three more expressions for  $T_a/T_b$  all complicated and not giving the desired linear relation.

The point here discussed was originally mentioned by Findlay,<sup>1</sup> who showed it however by using relations only one of which was according to the non-symmetrical form (3), the other being according to the symmetrical form (2).

No doubt many sets of observed points would fit either of the forms fairly well on account of the flatness of the reciprocal curve for the short range usually covered, and the inevitable observational irregularities. However, the fact that the forms (1) or (2) permit of reversal and interchange makes them preferable if for no other reason.

Similar remarks apply to laws of the same form as (2) announced<sup>2</sup>

<sup>1</sup>Zeit. phys. Chemie, Vol. 42, 1902, p. 110.

<sup>2</sup>Roy. Soc. Proc., Vol. 69, 1902, p. 471.

by Findlay for both chemical solubilities and equilibrium constants as functions of absolute temperature, instead of vapor pressures.

LATENT HEAT RATIO LAWS.

By differentiating (1) with respect to  $p$ , we obtain an expression which forms the basis of further relations

$$\frac{T_a^2 \frac{dp}{dT_a}}{T_b^2 \frac{dp}{dT_b}} = c.$$

For future purposes we write this

$$\frac{\frac{1}{c} \frac{dT_a}{dT_b}}{\frac{T_a}{T_b} \frac{dp}{dp}} = \frac{T_a}{T_b}. \quad (4)$$

We also use the well-known thermodynamic relation for saturated vapor

$$\frac{u}{r} = \frac{1}{AT} \frac{dT}{dp},$$

where  $A$  is reciprocal of mechanical equivalent of heat,  $r$  is latent heat of vaporization, and  $u$  is difference between specific volumes of vapor and liquid. Except near the critical point,  $u$  approximates to the specific volume corresponding to saturation pressure and temperature, given by the perfect gas law and the molecular weight. By substituting from the last relation in (4)

$$c \frac{u_a/r_a}{u_b/r_b} = \frac{T_a}{T_b}, \quad (5)$$

From (2) it follows that

$$\frac{\frac{1}{T_a} \frac{dT_a}{dp}}{\frac{1}{T_b} \frac{dT_b}{dp}} = 1 + \frac{k}{c} T_a, \quad (6)$$

$$\frac{u_a/r_a}{u_b/r_b} = 1 + \frac{k}{c} T_a, \quad (7)$$

$$\frac{Apu_a/r_a}{Apu_b/r_b} = 1 + \frac{k}{c} T_a. \quad (8)$$



In other words, the ratio of either of the quantities  $1/T \, dT/dp$ ,  $Apu/r$  or  $u/r$ , for two substances at the same vapor pressure has the same property as the ratio of absolute saturation temperatures, and is a linear function of the absolute temperature corresponding to the numerator. We remark that  $Apu/r$  is the ratio of external to total latent heat of vaporization, and that  $u/r$  is increase of volume per unit addition of latent heat. These laws, as in the case of the primary law, apply to subliming solids as well as to vaporizing liquids.

As stated, Ramsay and Young have shown that the constant  $k$ , and hence also  $k/c$ , is always very small, and is zero for homologous substances. Hence the quantities referred to are nearly alike for all substances at each vapor pressure, and exactly alike for homologous substances, as a consequence of the original law in the symmetrical form (1) or (2).

This was shown to hold for values of both  $Tdp/dT$  and  $r/u$  by actual computation of these quantities; and the essential features of the secondary law above referred to were given as independent empirical laws, by Ramsay and Young, prior to their announcement of the saturation temperature ratio law.<sup>1</sup> Referring to either of these quantities Ramsay and Young show that it is nearly the same for all substances at normal boiling point (saturation temperature corresponding to 760 mm. Hg vapor pressure) and that the ratio of values for any two given vapor pressures is nearly the same for all substances. These two relations are equivalent to the one given above, that values of  $1/T \, dT/dp$ , etc., are nearly the same for all substances at each vapor pressure.

Ramsay and Young also extended this approximate law to an exact form similar to (6)<sup>2</sup> giving it as an independent law however, and not as a consequence of the temperature ratio law, as here given. The evidence given by Ramsay and Young in support of the law is really evidence of the validity of the law (1) or (2).

In the paper alluded to, there are given tables from vapor pressure observations, of computed values of  $T \, dp/dT$ , and it is shown for a number of pairs of substances that the ratio  $T_b \, dp/dT_b \div T_a \, dp/dT_a$  for

<sup>1</sup> Phil. Mag., Vol. 20, series 5, 1885, p. 515.

<sup>2</sup> Phil. Mag., Vol. 21, series 5, 1886, p. 136.

various vapor pressures, is a linear function of  $T_a$ . This is exactly the law given by (6). In this paper the law is given that the ratio is a linear function of one of the absolute temperatures, but it is not stated as to whether this is the one corresponding to the numerator or denominator of the ratio. However, in all of the examples given, the ratio is shown to be a linear function of the temperature corresponding to the denominator of the form used in the paper, that is, the numerator when the form is as in (6).

#### LATENT HEAT LAWS.

By means of (7) we may compute  $u_b/r_b$  for all vapor pressures for a substance  $b$ , from the value for any one vapor pressure, and values of  $u_a/r_a$  and  $T_a$  for some standard substance  $a$  such as water vapor. Then values of either  $r_b$  or  $u_b$  can be computed if the other is known. As already stated,  $u$  is the difference between specific volumes of liquid and vapor at the saturation point and  $r$  is the latent heat of vaporization. The law is probably exact although it may be only a close approximation.

A rough approximation of simpler form may be deduced from the preceding considerations. We may write (5) in the form

$$\frac{r_a}{r_b} = c \frac{T_b/u_b}{T_a/u_a}.$$

Now  $u$  differs from the specific volume in the gaseous state by the specific volume of the liquid, usually a small quantity. In most cases the gaseous volume is nearly that corresponding to the perfect gas laws, and is directly proportional to the absolute temperature and inversely proportional to the molecular weight. Hence  $T_a/u_a$  and  $T_b/u_b$  are practically proportional to the molecular weights since the pressure is the same for both substances. That is, we have approximately  $r_a/r_b = \text{constant} = c \gamma_b/\gamma_a$ . Here  $r_a$  and  $r_b$  are latent heats of vaporization for two substances at the same vapor pressure, and  $\gamma_a$  and  $\gamma_b$  are molecular weights. The latent heat ratio is constant for each pair of substances for all vapor pressures. This law will give a general idea of the latent heat of any substance for all pressures from any one value and from known values for the same pressures for some standard substance.

As a further approximation we may substitute from (2) in the last expression, neglecting  $k$  since it is always small. This gives

$$\frac{r_a}{r_b} = \frac{T_a \gamma_b}{T_b \gamma_a},$$

or

$$\frac{r\gamma}{T} = \text{constant},$$

where  $\gamma$  is the molecular weight, or the "normal" density (at standard conditions, 760 mm. Hg and 0° C.), which is proportional to it;  $r$  is the latent heat of vaporization, and  $T$  is the corresponding saturation temperature. The constant is the same for all substances at a given vapor pressure. There is of course a different constant for each vapor pressure.

The approximate law thus rationally deduced was first given as an empirical law by Trouton,<sup>1</sup> being applied by him only for normal atmospheric pressure however. It is here extended to any pressure whatever.

#### EFFECT OF TEMPERATURE RATIO LAW ON GENERAL LAW FOR VAPOR PRESSURE.

A general relation between pressure and temperature of saturated vapor has long been sought without recognized success. No rational law holding from the supercooled region below the triple point up to the critical point, has ever been formulated. The temperature ratio law here discussed holds for this whole range however, so that it gives a condition which the general vapor pressure equation must satisfy almost if not quite exactly. This condition is that the vapor pressure  $p$  must be a function of  $(A - B/T)$  where  $T$  is absolute saturation temperature and  $A$  and  $B$  are two constants, different for each substance.<sup>2</sup> Other constants if they occur, are the same for all substances. That is to say, we must have  $p = f(A - B/T)$  or  $\log p = f(A - B/T)$ . This proposition is readily proven by noting that (1) may be written in the form

<sup>1</sup>Phil. Mag., Vol. 18 (series 5), 1881, p. 54.

<sup>2</sup>Aryton and Perry, Phil. Mag., Vol. 21 (series 5), 1886, p. 259.

$$A_2 - \frac{B_2}{T_b} = A_1 - \frac{B_1}{T_a}.$$

Since the constant  $k$  is always small,  $A_1$  and  $A_2$  are nearly alike. Hence in the general expression  $\log p = f(A - B/T)$  the constant  $A$  differs slightly for various substances and is exactly the same for homologous substances.

The mathematical form of statement that  $p$  is a function of  $A - B/T$  is as follows: Let us first suppose that we are considering various homologous substances, for which  $A$  is constant. Then  $p$  and  $A - B/T$  are each functions of the two independent variables  $B$  and  $T$ . Since by hypothesis  $p$  is also a function of  $A - B/T$ , we have from the mathematical "condition for functionality"

$$\left(\frac{dp}{dT}\right)_{AB} = -\frac{B}{T} \left(\frac{dp}{dB}\right)_{AT}.$$

In the same way, since  $A$  and  $T$  may be variable with constant  $B$ , we deduce the condition

$$\left(\frac{dp}{dT}\right)_{AB} = \frac{B}{T^2} \left(\frac{dp}{dA}\right)_{BT}.$$

A third equation can be formed, but it is not independent. The general vapor-pressure equation is the integral of these partial differential equations.

#### DIETERICI'S VAPOR PRESSURE LAWS.

Dieterici has proposed a vapor-pressure law equivalent to

$$7.4 p \frac{T_k dT}{T dp} = T$$

where  $T_k$  is the critical temperature. This gives as the relation between saturation temperatures  $T_a$  and  $T_b$  of two substances at the same vapor pressure

$$\frac{T_{ak} \frac{T_a}{T_b} \frac{dT_a}{dp}}{T_{bk} \frac{T_b}{T_a} \frac{dT_b}{dp}} = \frac{T_a}{T_b}.$$

By comparison with (4), this law gives the value  $T_{ak}/T_{bk}$  for the constant  $c$ , so that (1) becomes

$$\frac{1}{T_b} = \frac{T_{ak}}{T_{bk}} \frac{1}{T_a} + k$$

or

$$\frac{1/T_b - k}{1/T_a} = \frac{T_{ak}}{T_{bk}}$$

where  $T_{ak}$  and  $T_{bk}$  are critical temperatures of the substances  $a$  and  $b$ .

If we plot reciprocals of absolute saturation temperatures corresponding to the same vapor pressure against each other, as is done in the chart of the previous article,<sup>1</sup> we obtain straight lines, as already shown. According to Dieterici's law the tangents of the angles of these lines with the horizontal will be proportional to the critical temperatures of the substances whose values of  $1/T$  are plotted horizontally. Inspection of the chart shows that in a general way this is true, and that the less the angles the lower the critical temperatures. However, quantitative test of the law by measurement of the tangents of the angles of the vapor-pressure lines and comparison with observed critical temperatures shows that there is no approach to proportionality, and that the law is only a very roughly approximate one.

Dieterici's expression for vapor pressure when integrated gives a law of the form

$$\log p = A - \frac{B}{T}.$$

This is the simplest form of law agreeing with the conditions imposed by the temperature ratio law. However, as is well known, such a form does not at all represent observations, so that Dieterici's expressions are not exact.

#### VAPOR PRESSURE FORMULAS.

The temperature ratio law enables deduction of a law for vapor pressure of any substance from any of the empirical expressions for water-vapor pressure which can be put in the form  $\log p = f(A - B/T)$ . This was done in the preceding article for Rankine's law.<sup>2</sup> However this law does not give a very good representation of observations. On the contrary a law for pressure

<sup>1</sup> PHYS. REV., Vol. 16, p. 358.

<sup>2</sup> PHYS. REV., Vol. 16, p. 361.

of water vapor of a form suggested by Roche<sup>1</sup> but reconstructed and called by Regnault Formula K<sup>2</sup> gives excellent agreement with observations. The law is

$$p = a\alpha^{\frac{T-253}{1+m(T-253)}}.$$

Regnault gives

$$\log \alpha = 0.03833818 \quad \log a = 1.9590414 \quad m = 0.004788221.$$

This formula agrees very closely with the results of experiments by Regnault and Ramsay and Young<sup>3</sup> and also with experiments at higher temperatures up to the critical point.<sup>4</sup> In the preceding table of saturation temperatures of water vapor a column of values from this Formula K is given. They agree with values computed from methyl alcohol observations within a few tenths of a degree. In fact this formula agrees with any one series of observations as well as the various observers agree among themselves. It probably best represents our present experimental knowledge of water-vapor pressure from below triple point to the critical point.

This formula may be reduced to the general form consistent with the temperature ratio law, and then takes the form (exactly equivalent to the original form given above)

$$\log p = 45.8372 - (0.0264052 - 1.16589/T)^{-1}.$$

Here  $p$  is the pressure of water vapor in mm. Hg, and  $T$  is the corresponding absolute centigrade saturation temperature. For any other vapor we have as an expression which represents observations accurately

$$\log p = 45.8372 - (A - B/T)^{-1},$$

where  $A$  and  $B$  are constants for each substance.  $A$  is always close to 0.0264052 and has the same value for all substances of a homologous series. In both of these formulas the first constant becomes 44.1236 for pressure in lbs. per sq. in.

There is one class of proposed vapor-pressure formulas which

<sup>1</sup> Memoires de L'Institut, etc., Vol. 10, 1831, p. 227. As given by Roche, the formula does not agree at all with modern observations.

<sup>2</sup> Memoires de l'Institut, etc., Vol. 21, 1847, p. 613.

<sup>3</sup> Phil. Trans., Vol. 183, 1892, p. 111.

<sup>4</sup> Engineering, Vol. 83, January 4, 1907.

cannot be reduced to a form consistent with the temperature ratio law. These have the general form

$$\log p = A + B/T + C \log T.$$

This and similar relations have been deduced rationally by Rankine<sup>1</sup> and Gibbs<sup>2</sup> and others, but so far as the writer's knowledge extends, always for the region at a distance from the critical point, that is, for liquid volume small compared with vapor volume. This form is therefore not rational for the whole region from triple point to critical point. On the contrary the temperature ratio law applies to this whole region, so that concordance with the partial law above is not to be expected.

By empirically selecting the constants to suit, the above form may be applied to the whole region, and fair coincidence is found, since there are three arbitrary constants to choose. However, since this form is empirical and not rational when extended to the whole region, and since it gives no better representation of observations than the Roche law previously discussed, the Roche form is preferable since it is in accord with the temperature ratio law.

Comparison may be made of the temperature ratio law here discussed and the "law of corresponding states." Both laws give a relation between saturation temperatures for two substances, the former for the same vapor pressure, and the latter for vapor pressures bearing the same ratio to the critical pressures. The two laws are therefore distinct.

#### REDUCTION OF VAPOR PRESSURE OBSERVATIONS.

The form and exactness of the Roche law or "Formula K" suggests a modification of the method used in obtaining the charts of the previous article. We have for any vapor

$$A - B \frac{1}{T} = \frac{1}{45.8372 - \log p}$$

where  $p$  is vapor pressure in mm. Hg (constant is 44.1236 for lbs. per sq. in.), and  $T$  is the corresponding absolute centigrade saturation temperature. Hence if  $1/T$  is plotted against  $1/(45.8372 - \log p)$

<sup>1</sup> Phil. Mag., Vol. 31, series 4, 1866, p. 199.

<sup>2</sup> Scientific Papers (Thermodynamics), p. 152, footnote.

from observed values, the points should lie in a straight line, except for observational irregularities. The observations may be smoothed by readings from the straight line best representing the points, or by computation from the formula obtained by use of the numerical values of  $A$  and  $B$  obtained from the straight line.

The principle at the basis of this method is exactly the same as that used in obtaining the charts of the preceding article. Here however, the ordinates giving the vapor-pressures are obtained by formula instead of from tables of water vapor pressure.