THERMODYNAMIC PROPERTIES
OF VAPORS

THESIS

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By introducing new properties of state and an ideal system, that is, a perfect vapor, the representation of the thermodynamic properties of vapors is simplified. The field of state reduces to one curve of state which requires in the experimental investigation of vapors only as many measurements as are necessary for the determination of this curve. The equations of state are found more easily, the calculations required to determine the vapor tables are reduced, and a simple formula for the external work is found. An analytic investigation of the equilibrium of a liquid with its vapor shows how the vapor-pressure curve can be found from the equation of state.

There are essentially three ways to investigate the properties of thermodynamic systems. In the first case, the properties are derived from experiments made with real substances. In the second case, the properties are determined from a molecular theory, on which the system is based. In the third case, the properties are deducted from a definition, by which an ideal system is created. This paper will use the latter way to introduce an ideal system, the qualities of which are in good agreement with the qualities of actual vapors. Reliable tables and equations of state for vapors can be established on the basis of such a system even if only a few experimental data are available. The application of this method to several substances will be demonstrated by examples.

NOMENCLATURE

The following symbols are used in this paper:

- \( p \) = pressure
- \( v \) = volume
- \( u \) = internal energy
- \( h \) = enthalpy
- \( s \) = entropy
- \( T \) = absolute temperature
- \( f \), \( \theta \), \( \tau \), \( \phi \), \( z \) = elementary properties of state
- \( f \) = number of degrees of freedom
- \( c_v \) = specific heat at constant volume
- \( c_p \) = specific heat at constant pressure
- \( A \) = isothermal work
- \( L \) = adiabatic work
- \( \beta \) = gas constant
- \( \Psi \) = characteristic function
- \( \zeta \) = thermodynamic potential
- \( a, b, \phi \) = functions of equilibrium
- \( x, y, z \) = functions of state
- \( \alpha, \beta, \omega \) = auxiliary functions

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors, and not those of the Society.
If we substitute
\[ x^* = p^* v^{x^* + 1} \]

it follows that
\[ ds = \frac{dx - x^* dv}{\theta} \]

If \( ds \) is a total differential, the following equation must be satisfied
\[ \frac{\partial}{\partial x} \left( x^* \right) = \frac{\partial}{\partial v} \left( x^* \right) \]

From Equation [6]
\[ \frac{\partial x}{\partial v} = \pi^* - \theta \frac{\partial x^*}{\partial \theta} \]  
and from Equation [4]
\[ \epsilon = (1/\alpha) (x + x^*) \]

\[ \frac{1}{\alpha} \left( \frac{\partial x^*}{\partial v} + \frac{\partial x^*}{\partial \theta} \right) = x^* - \theta \frac{\partial x^*}{\partial \theta} \]

2—The Perfect Vapor

Equation [9] is a general relation between two dependent variables which holds for every thermodynamic system, but is not sufficient to recognize its condition. For an ideal system with a limiting condition in which Equation [9] contains only one dependent variable, this modified equation yields a relation for the condition of the system. The limiting condition is
\[ \frac{\partial x}{\partial v} = 0 \]

The perfect vapor defined by Equation [10] has the characteristic that one of the elementary properties of state depends only on one independent variable. This is in remarkable agreement with the behavior of actual vapors. Simple laws will also be found for the other properties. By substituting Equation [10] into Equation [9]
\[ \theta \frac{\partial x^*}{\partial \theta} + \frac{1}{\alpha} \frac{\partial x^*}{\partial v} = x^* \]

Integration gives:
\[ x^* = f(\theta) \left( \frac{\theta}{\theta_0} \right) \]

Using Equation [5] gives
\[ x^* = \theta f(T) \]

where \( f(T) \) is an arbitrary function of the temperature. The relations between the thermal and calorific properties of the perfect vapor are, according to Equation [8]
\[ \epsilon = \frac{1}{\alpha} \left[ x + \theta f(T) \right] \]

and
\[ u = \frac{1}{\alpha} \left[ px + T f(T) \right] \]

Being a function of temperature only, \( f(T) \) can be determined for an arbitrary pressure. If we choose the pressure zero, the intermolecular forces will disappear and the perfect gas law will be fulfilled, whence \( px = RT \).

Then the internal energy at \( p = 0 \) is given as
\[ u = (1/\alpha) RT + (1/\alpha) T f(T) \]

According to the previous assumption that the translation and rotation is fully activated and that the oscillation is partially activated, \( (1/\alpha) RT \) is the contribution by the translation and rotation to the internal energy of the perfect vapor. Thus, \( (1/\alpha) T f(T) \) is the contribution due to the oscillation.

Since the variation of the energy of oscillation with pressure is negligible, the quantity \( (1/\alpha) T f(T) \) represents the energy of oscillation at arbitrary pressures.

Then from Equation [11]
\[ x^* = \alpha x^* \theta \]

from Equation [12]
\[ u = (1/\alpha) px + u_{oct} \]

and from Equation [2]
\[ u_{oct} = (1/\alpha) px - RT \]

Equation [15] can be considered as characteristic for the perfect vapor.

Making simplifying assumptions which are exact enough for technical applications, the specific heat of oscillation for every degree of freedom can be written as
\[ c_{oct} = R \left( \frac{T}{\theta_0} \right) \phi^{1/2} \phi^{1/2} \]

where \( \theta_0 \) represents the "characteristic temperature" of the oscillation. By integration and addition over the \( f_0 \) degrees of freedom, the contribution of the oscillation to the internal energy is
\[ u_{oct} = R \phi = \sum_{T}^{T_0} \theta_0 \]

where \( \phi \) represents the individual terms in the summation. Therefore, from Equation [14]
\[ u = \frac{1}{\alpha} px + R \phi \sum_{T}^{T_0} \theta_0 \]

Introducing the enthalpy \( h = u + px \), we obtain
\[ h = \frac{1}{\alpha} px + R \phi \sum_{T}^{T_0} \theta_0 \]

The characteristic function
\[ \Psi = z - (u/T) \]

has the differential
\[ d\Psi = ds - \frac{Tdu - udT}{T^2} \]

Substituting Equation [1] gives
\[ d\Psi = \frac{u}{T^2} dT + \frac{p}{T} dv \]

In Equation [18] the coefficient of \( dT \) is \( \partial \Psi / \partial T \), and the coefficient of \( dv \) is \( \partial \Psi / \partial v \), which yields the relations
\[ u = T^2 \frac{\partial \Psi}{\partial T} \quad \text{and} \quad p = T \frac{\partial \Psi}{\partial v} \]
By substitution of Equation [19] into Equation [16], the following differential equation for \( \Psi \) is obtained

\[
\frac{\partial \Psi}{\partial T} = \frac{1}{\alpha} \frac{\partial \Psi}{\partial \theta} + R \sum_{i=1}^{n} \frac{\theta_i}{\theta_i + 1} \frac{\partial \theta_i}{\partial T}
\]

which has the integral

\[
\Psi = F(T\theta^a) + R \sum_{i=1}^{n} \frac{\theta_i}{\theta_i + 1} \log \frac{\theta_i}{\theta_i + 1}
\]

The function \( \Psi \) determines the entire behavior of the system. \( F(T\theta^a) \) is an arbitrary function of the elementary property \( \theta \) only, while the second term is a function of the temperature only; \( F \) must be determined for each substance by experiment or individual theory. The definition of the perfect vapor does not include any limitation whatsoever regarding the character of the function \( F(\theta) \). Its significance results from the following derivations:

Equation [19] gives

\[
p = \alpha T \theta^a - 1 F'(T\theta^a)
\]

which yields

\[
\frac{\psi}{\theta} = \frac{p \theta^{a+1}}{T \theta^a} = \alpha \theta F'(\theta)
\]

when integrated

\[
F(\theta) = \frac{1}{\alpha} \int \frac{\psi}{\theta} d\theta
\]

therefore

\[
\Psi = \frac{1}{\alpha} \int \frac{\psi}{\theta} d\theta + R \sum_{i=1}^{n} \frac{\theta_i}{\theta_i + 1} \log \frac{\theta_i}{\theta_i + 1}
\]  

As soon as \( \pi(\theta) \) and the \( \theta_i \) are given, the function \( \Psi \) is entirely determined.

The further characteristic qualities of the perfect vapor can be found:

(a) The specific heats can be written as

\[
c_v = \left( \frac{\partial u}{\partial T} \right)_v = \frac{\alpha + 1}{\alpha + 1} p \frac{\partial \theta}{\partial T} + c_{\text{mol}}
\]

from Equation [16], and

\[
c_p = \left( \frac{\partial h}{\partial T} \right)_p = \frac{\alpha + 1}{\alpha} p \frac{\partial \theta}{\partial T} + c_{\text{mol}}
\]

from Equation [17].

(b) The derivatives of the natural properties of state are

\[
\frac{\partial u}{\partial v} = \frac{\partial (pv)}{\partial v}
\]

from Equation [16], and

\[
\frac{\alpha}{\alpha + 1} \frac{\partial h}{\partial p} = \frac{\partial (pv)}{\partial p}
\]

from Equation [17].

With \( \frac{\partial u}{\partial v} = T \frac{\partial p}{\partial T} - p \), which follows from the Second Law, we obtain from Equation [12]

\[
p + \frac{\partial p}{\partial v} = \alpha \left( T \frac{\partial p}{\partial T} - p \right)
\]

or

\[
T \frac{\partial (pv)/T}{\partial T} = \frac{\partial (pv)/T}{\partial v}
\]

From Equation [21]

\[
\frac{\partial c_v}{\partial T} = \frac{\partial (pv)/T}{\partial v}
\]

or, since \( c_{\text{mol}} \) does not depend on \( v \)

\[
T \frac{\partial c_v}{\partial T} = \frac{\partial (pv)/T}{\partial v}
\]

For the perfect vapor

\[
c_v - c_{\text{mol}} = c_v + c_{\text{rot}} + c_{\text{mol}} = (R/\alpha) + c_{\text{mol}}
\]

Accordingly

\[
T \frac{\partial c_v}{\partial T} = \frac{\partial (pv)/T}{\partial v}
\]

As a consequence of the fundamental condition of the perfect vapor Equation [10], there exist relations of Equations [21] to [28], inclusive, between the natural properties of state. These equations are the only limitations for the properties of that system. No limitations are made of the value of these properties or their derivatives. In this manner, the perfect vapor differs from the perfect gas, which has, in addition to Equation [10], the limiting condition \( \frac{\partial u}{\partial v} \) = 0 for the value of a certain derivative. The fundamental property of the perfect vapor, from which all other properties derive, is that the elementary property of state \( x \) is a function of \( \theta \) only.

3—TECHNICAL VAPORS DESCRIBED AS PERFECT VAPORS

The agreement of the thermodynamic properties of vapors used in technical processes with those derived in Section 2 for the perfect vapor can easily be checked by the results of Equations [10] and [17]. This means (a) if we represent the thermal properties on a \( x, \theta \) chart, all points of the vapor state will coincide on one curve, since \( x \) depends on \( \theta \) only; and (b) the quantity \( h = \frac{1}{\alpha} + (1/\alpha) \frac{\partial v}{\partial \theta} \) is a function of temperature only, which has the value given in Equation [17]. We proceed now with a verification of the properties in (a) and (b) for several substances.

Steam: \( \alpha = 1/\alpha \). The calculations are based on the skeleton table (1)\(^3\) of 1935 for the tolerance \( \pm 0 \). From this table, we obtain the well-known \( pv/RT \), \( t \) chart, shown in Fig. 1, from which those points for saturated and superheated steam which are indicated by circles were selected to be represented in a \( x, \theta \) chart, shown in Fig. 2. These points cover a range from an approximately gaseous condition to a condition which deviates 75 percent from the gas law. These points coincide almost exactly into a single curve, which for great values of \( \theta \) approximates the straight line \( x = R\theta \), the latter characterizing the perfect gas law. The values for the critical point are

\[
\theta_c = 97.123 \text{ m deg C/kg}^{1/3}; \quad x_c = 1142.8 \text{ m}^2/\text{kg}^{1/3}
\]

The points for saturated water are marked as a supplement to the vapor. We see that only for very small volumes—about \( v < 2v_c \)—the points will not coincide into one curve. The tangent

\(^3\) Numbers in parentheses refer to the Bibliography at the end of the paper.
## Table 1: Values of \( A - 4p_v \) for Steam

<table>
<thead>
<tr>
<th>Temperature, ( T ), °C</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
</tr>
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<td>100</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Temperature, } T, \text{ °C} & \quad 250 & 300 & 350 & 400 & 450 & 500 & 550 \\
\text{Pressure, } p_v, \text{ kg/cm}^2 & \quad 203854 & 203713 & 203799 & 203912 & 204129 & 204447 & 204312 & 204315 \\
& & & & & & & & \text{Values of } A - 4p_v \\
\end{align*}
\]

Fig. 1 Deviation of a Water Vapor from the Perfect Gas

Fig. 4 Enthalpy of Steam Compared with That of a Perfect Vapor

Fig. 2 and 3 Elementary Properties of State of Steam
of the \( \pi, \theta \) curve at the critical point has the same slope as the gas line \( \pi = R\theta \).

From Fig. 2, the curve \( \pi/R\theta = f(\theta) \) can be derived. This curve is shown in Fig. 3 and can be used to establish an empirical equation of state. It indicates how the points in Fig. 1 coincide into a single curve, if one chooses \( \theta \) instead of \( T \) as abscissa; the ordinate is the same, since according to Equation [5] \( \pi/R\theta = pv/RT \).

The quantity \( h - 4p \) has the values given in Table 1, which are derived from the skeleton tables (1) and expressed in m kg/kg.

In the large range covered by these tables, \( h - 4p \) is, at constant temperature, almost independent of pressure except the values at very high pressures. Most points from the table are marked in Fig. 4 together with the curve \( \int(c_p - 4R)dT \) according to the \( c_p \) data by Justi and Lüder (2). The constant of integration is fixed to make the saturation curve pass through the 0 C point of Table 1.

We recognize from the figure that the deviation of the observed values from the curve is very small. Even the variation of \( h - 4p \) with the temperature amounts only to a few per cent. The reason is the small variation of \( \int(c_p - 4R)dT \) compared with the great value of the constant of integration. Thus, we obtain as an approximation

\[
h = a_0 + a_1p
\]

which relation had already been found in an empirical manner (3). Thus we see that steam is in close agreement with the condition of the perfect vapor.

---

**Fig. 5 Elementary Properties of State of Carbon Dioxide**

*Carbon Dioxide: \( \alpha = 1/\beta \).* Fig. 5 shows the \( \pi, \theta \) chart, calculated from Amagat's values. For this substance also the points of state coincide, in general, into one curve when the volume is not too small. Since the volume of carbon dioxide is not measured as accurately as that of steam, the points scatter a little more than those on the steam chart. The chart covers the range from 40 to 140 kg/cm² and from -20 C to +50 C. In the whole range, the deviation from the gas law is very considerable as shown by the straight line \( \pi = R\theta \). An empirical equation of state, which holds for pressures up to 40 kg/cm² (4) is

\[
v = \frac{RT}{p} - 0.0825 + \left(1.225 \times 10^{-7}\right)p
\]

\[
R = 19.273 \text{ m kg/kg deg C} \quad [v] = \text{m}^3/\text{kg} \quad [p] = \text{kg/m}^2.
\]

According to the Second Law, we obtain the enthalpy by integrating the equation

\[
\frac{\partial h}{\partial p} = v - T \frac{\partial v}{\partial T} = \frac{\pi - 4p}{R\theta}
\]

which gives

\[
h = \int(c_p - \frac{7}{2}R) = \frac{8.3724p + 0.06216p^2}{(T/100)^{7/2}}
\]

where \( p \) is to be substituted in kg/cm² and \( \int \) is the temperature function to be introduced by the integration. Then we obtain from Equation [17]

\[
h = \frac{7}{2}p = \int(c_p - \frac{7}{2}R) = \frac{1.61p - 0.03826p^2}{(T/100)^{7/2}}
\]

The first term on the right-hand side corresponds to the value of \( h - (7/2)p \) for the perfect vapor, according to Equation [17]. The second term on the right-hand side denotes the deviation of the actual CO₂ vapor from the perfect vapor. The constants used in the calculation of \( c_p \) are

\[
\theta_1 = \theta_2 = 960 \text{ C} \quad \theta_3 = 1830 \text{ C} \quad \theta_4 = 3280 \text{ C}
\]

Fig. 6 represents this equation where the constant of integration is so fixed that \( \int(c_p - (7/2)R)dT = 0 \) at the freezing point \( T = 216.8 \text{ C abs} \). The addition of the second term of the equation results in the scattering of the actual points of state about the theoretical curve. The figure shows that the scattering is very slight and that the CO₂ vapor can be represented with sufficient accuracy as a perfect vapor.

---

**Fig. 6 Enthalpy of CO₂ Vapor Compared With That of a Perfect Vapor**

*Hydrocarbons: \( \alpha = 1/\beta \).* Edmister has succeeded (5) in representing 17 hydrocarbons with close approximation by a joint equation in reduced properties of the type

\[
v = \frac{RT/p}{} - b
\]

Dividing the quantities \( T, p, b \) by their respective values \( T_k, p_k, b_k \) for the critical point, yields

\[
\frac{v}{b} = \frac{RT_k}{p_k} - b_k
\]
where \( b_1 \) is the same function of both \( T_r \) and \( p_r \) for the 17 substances examined, and the average value of \( RT_k/p_kb_k \) is 1.368, which happens to be the correct value of propane (C\(_3\)H\(_8\)).

We apply the laws of the perfect vapor to this substance. For this case, let

\[
\alpha_r = T_r \left( \frac{v}{b_0} \right)^{1/3} \quad \text{and} \quad \xi_r = p_r \left( \frac{v}{b_0} \right)^{1/3}
\]

The experimental data determine the \( \xi_r, \alpha_r \) chart of Fig. 7 where the gas condition is represented by the straight line, \( \xi_r = (RT/pb)h_\alpha \). The figure contains the range of \( 0.2 < p_r < 2.5 \) and \( 0.8 < T_r < 2.5 \) and shows that within these limits, the points of state are approximately located on a single curve.

By means of the statements made in the reported paper (5), we can write Equation [17] as shown in the following paragraph.

The specific heat of propane in the gas condition is

\[
c_p = 4.09 + 0.0432T \ \text{Kcal/mol deg C}
\]

from which the enthalpy in the gas condition can be obtained by integration as

\[
h_0 = 4.09T + 0.0216T^2 + h' \ \text{Kcal/mol}
\]

or

\[
h_0 = 1513T_r + 2955T_r^3 + h' \ \text{Kcal/mol}
\]

If \( \Delta h \) denotes the difference in enthalpy between the gas condition and the condition at any pressure, Equation [17] is written as

\[
h_0 - p_kb_0 \left( \frac{\Delta h}{p_kb_0} + 4 \frac{p}{p_k} \frac{v}{b_0} \right) = h_0 - 4RT + h'
\]

where \( \Delta h/p_kb_0 \) is again the same function of both \( p_r \) and \( T_r \) for the 17 hydrocarbons.

If we suppress \( h_0 \)

\[
\frac{\Delta h}{p_kb_0} + 4 \frac{v}{p_k} \frac{v}{b_0} = 4 \left( \frac{RT}{pb} \right) T_r - h'
\]

This equation is represented in Fig. 8 for propane where the constant of integration is so fixed that \( h' = 0 \) at the critical point. The critical data of propane are \( T_k = 369.9 \ \text{Cabs}; \ p_k = 43.4 \ \text{kg/cm}^2; \ v_k = 0.195 \ \text{m}^3/\text{mol}; \ b_k = 0.528 \ \text{m}^3/\text{mol}. \) Furthermore, the molecular weight \( M = 44.06 \ \text{kg/mol}, \) and the gas constant \( R = 848 \ \text{m kg/mol deg C}. \)

Fig. 8 shows also that the observed values scatter only slightly about the straight line calculated from the foregoing equation for the perfect vapor. Due to the rough approximation in representing the 17 substances by the same law, we cannot expect the points to coincide better on the straight line. We recognize from Figs. 7 and 8 that hydrocarbon vapors in general follow the laws of the perfect vapor.

The advantages which result from the possibility of representing technical vapors as perfect vapors consist in great simplification of the preparatory work required to establish equations of state and tables.

Since the whole field of natural properties reduces to one curve of elementary properties, it is necessary to determine by experiments only as many points as are needed to determine this curve. Then, all other states can be calculated from this curve. By this method we can avoid part of the measurements at high pressures.

The calculation of the calorific properties from the thermal properties will also be simple. From Equation [17] it follows, that an additional temperature function only must be given to calculate the enthalpy for given values of \( p \) and \( v. \) This function can either be given empirically or can be calculated from the \( \Theta \) values, which are known by spectroscopic measurements for many substances.

4—Empirical Equation of State for Vapors

The possibility of representing the state of vapors by one curve facilitates the formation of an empirical equation of state. Due to its characteristic form, the function \( \pi/R\Theta = f(\Theta) \) is most suitable for the analytic representation. The curve of this function belongs to the type

\[
y = \frac{1/x}{e^{1/x} - 1} \quad \text{[29]}
\]

where \( x \) must be represented as such a function of \( \Theta \) that it from Equation [29] gives the same value as \( y = \pi/R\Theta \) from the curve of state, shown in Fig. 3, for the same value of \( \Theta. \)
To find this function \( x = f(\theta) \) we plot the values \( x \) in Equation [29] against those values \( \theta \) of the curve of state, shown in Fig. 3, which belong to the same ordinate. Fig. 9 shows the curve \( x = f(\theta) \) for steam which can be represented with great exactness by

\[
x = \left( \frac{x}{\theta_0} \right)^4 \quad \text{[30]}
\]

The points of state in the figure are the same as in Fig. 1. They scatter very slightly about the straight line which is for two thirds of all points within the tolerance of the skeleton table if \( \theta_0 \) is taken equal to 136.5 m deg C/kg\(^{1/3}\). For the other points the deviation also amounts, in the most unfavorable case, to a small percentage. Since the measurements of volume of most vapors have small errors we can expect that the method described here for steam can be applied to the equations of state of other substances.

From Equations [29] and [30] we obtain

\[
\frac{\pi}{R \theta^3} = \frac{\theta}{e^{(\theta/\theta_0)^1} - 1} \quad \text{[31]}
\]

The empirical equation of state then is expressed in natural properties by

\[
pv = R \left( \frac{\theta}{e^{(\theta/\theta_0)^1} - 1} \right) \quad \text{[32]}
\]

Equation [32] holds for the entire range of vapor when \( v > 2v_c \). With the exception of the gas constant, this equation contains only one other constant, \( \theta_0 \). It follows from Equation [31] that we must determine \( \int \left( \frac{x}{\theta} \right) d\theta \) in order to know the value of the characteristic function. It follows from Equation [31] that

\[
\pi \frac{d\theta}{\theta} = R \frac{\theta}{e^{(\theta/\theta_0)^1} - 1} - \frac{R}{3} \frac{\theta_0}{e^{(\theta/\theta_0)^1} - 1}
\]

the integral of which is

\[
\int \pi \frac{d\theta}{\theta^3} = \frac{R}{3} \log_e \frac{e^{(\theta/\theta_0)^1} - 1}{\theta_0}
\]

Thus, we obtain

\[
\psi = R \log_e \frac{e^{(\theta/\theta_0)^1} - 1}{\theta_0} + R \sum_{1}^{f_1} \log_e \frac{e^{(\theta/T)^1} - 1}{\theta_0} \quad \text{[33]}
\]

as the characteristic function.

Hence, from Equation [19], the energy of the perfect vapor is obtained as the empirical equation

\[
u = 3RT \frac{\theta}{e^{(\theta/\theta_0)^1} - 1} + R \sum_{1}^{f_1} \frac{\theta_1}{e^{(\theta/T)^1} - 1} \quad \text{[34]}
\]

Finally, the entropy results from the Second Law as

\[
s = \psi + \frac{\mu}{T}
\]

From Equations [33] and [34]

\[
s = R \log_e \frac{e^{(\theta/\theta_0)^1} - 1}{\theta_0} + \frac{R}{3} \frac{\theta_0}{e^{(\theta/\theta_0)^1} - 1} + \frac{R}{3} \sum_{1}^{f_1} \log_e \frac{e^{(\theta/T)^1} - 1}{\theta_0} + R \sum_{1}^{f_1} \frac{\theta_1}{e^{(\theta/T)^1} - 1} \quad \text{[35]}
\]


5—Establishment of the Vapor Table

If we start from the characteristic function to describe the thermodynamic properties of a vapor, it follows from Equation [19] that pressure is the only thermal property which can be represented as an explicit function of temperature and volume. It is not possible to obtain volume or temperature as an explicit function of the other two properties of state. In vapor tables, the volume is to be represented as a function of pressure and temperature. A solution of this problem by an empirical method results in an analytic expression, which becomes more complicated for greater validity and exactness of the formula. However, the problem presents a simple solution for a system of the type of Equation [33].

The equation \( p = f(T, \psi) \), belonging to Equation [33], is represented in Equation [32]. Multiplying both sides of Equation [32] with \( \theta_0^4/T^4 \), we obtain, with the aid of Equation [30]

\[
\left( \frac{\theta_0}{T} \right)^4 \frac{p}{RT} = \frac{1}{e^{1/x} - 1} \quad \text{[36]}
\]

Moreover, from Equations [30] and [5]

\[
v = \pi(\theta_0/T)^4 \quad \text{[37]}
\]

Thus, it is only necessary to establish a table of the function

\[
x = \frac{1}{e^{1/x} - 1} \quad \text{[38]}
\]

to determine the volume for the given pressure and temperature.

First, calculate the left side of Equation [36] to obtain \( x(z) \). Taking the value \( x \) from the table, calculate \( v \) according to Equation [37]. After finding the \( p, v, T \) values, the temperature function of Equation [17] must be obtained from experimental data, from which equation the enthalpy can be calculated. The entropy is obtained from Equation [35].

In the equations used for the calculation of \( s, h, \) and \( s \), the same functions which belong to the following types, are used

\[
\frac{1}{x} = \frac{1}{e^{1/x} - 1} \quad \frac{1}{e^{1/x} - 1} \quad \log_e \frac{e^{1/x} - 1}{e^{1/x} - 1}
\]

Once tables for these functions are made, the calculation of vapor tables presents no difficulty. An assumption similar to that of Equation [30] will be sufficient, in general, if the neighborhood of the critical point is avoided. By modification of \( \theta_0 \) in the neighborhood of the saturation line, the accuracy required by the International Steam Tables can be maintained.

6—Isothermal Work of Vapors

For a vapor which satisfies Equation [33], the following is obtained

\[
p = \psi \frac{\theta_0^4/T^4}{e^{(\theta/\theta_0)^1} - 1} \quad \text{[38]}
\]

or

\[
p = \frac{RT^4}{\theta_0^4} \frac{(\theta_0/\theta)^4}{e^{(\theta/\theta_0)^1} - 1} \quad \text{[39]}
\]

The isothermal work of expansion can be found from

\[
\int dA = \int pdv = \int \frac{RT^4}{\theta_0^4} \frac{(\theta_0/\theta)^4}{e^{(\theta/\theta_0)^1} - 1} dv
\]

By substituting Equation [30] for \( T = \text{constant} \)

\[
\int dA = \int \frac{RT}{e^{1/x} - 1} dx
\]
the integral of which for the work of expansion, from the initial state to the final state, is

\[ A = RT \log \frac{1 - e^{-\frac{1}{\gamma \mu_1}}}{1 - e^{-\frac{1}{\gamma \mu_2}}} \]

Substituting the original variables, the isothermal work of expansion is found as

\[ A = RT \log \frac{1 - e^{-\frac{(\theta_0/T)^{(1/n)}}}{1 - e^{-\frac{(\theta_0/T)^{(1/n)}}}}}{0.39} \]

In the limiting case, where the vapor condition approximates the gas condition—large values of \( T \) or \( \varphi \)—the exponential function can be developed in a series which can be terminated after the linear term, thus obtaining the approximation

\[ e^{-\frac{(\theta_0/T)^{(1/n)}}}{1 - e^{-\frac{(\theta_0/T)^{(1/n)}}}}{0.39} \]

In this case

\[ A = RT \log \frac{\varphi_2}{\varphi_1} \]

which is the well-known law for the work of expansion of a perfect gas. It is of interest to examine the manner in which the external work of Equation [39] varies if the volumes \( V_1 \) and \( V_2 \) remain the same, but the temperature \( T \) is changed by \( dT \) and then \( T \) is allowed to approach zero.

By differentiation at constant volume, from Equation [39]

\[ \frac{dA}{dT} = R \log \frac{1 - e^{-\frac{(\theta_0/T)^{(1/n)}}}{1 - e^{-\frac{(\theta_0/T)^{(1/n)}}}}}{0.39} \]

or

\[ \frac{dA}{dT} = \frac{R \log \varphi_2 - R \log \varphi_1}{\varphi_2 - \varphi_1} \]

The first term in Equation [41] is

\[ R \log \frac{\varphi_2}{\varphi_1} \]

Then, if \( T \) approaches zero, each term in Equation [41] approaches zero. Accordingly

\[ \lim_{T \to 0} \frac{dA}{dT} = 0 \]

To show the application of Equation [39], calculate the work of isothermal expansion for steam at 400°C from 200 kg/cm² to 100 kg/cm² (A-B in Fig. 1), which is a range where the deviation from the gas law is very large.

For a check, first calculate the amount of the work from the V.D.I. steam tables.

In the final state:

\[ \varphi_2 = 0.02710 \text{ m}^3/\text{kg} \]
\[ h_2 = 676.5 \text{ Kcal/kg} \]
\[ s_2 = 1.3327 \text{ Kcal/kg deg C} \]
\[ u_2 = 628.9 \text{ Kcal/kg} \]

According to the Second Law, the work of isothermal expansion is

\[ A = T(s_2 - s_1) - (u_2 - u_1) \]

With these values, it follows that

\[ A = 54.9 \text{ Kcal/kg} \]

According to Equation [39], taking \( \theta_0 = 138.5 \text{ m deg C/kg}^{1/3} \) and \( \varphi_1, \varphi_2 \) from the V.D.I. steam tables

\[ \begin{align*}
A &= 74.2 \log \frac{1 - e^{-0.098337}}{1 - e^{-0.01031}} = 74.2 \log e^{0.098337} = 74.2 \log 2.0040 = 54.8 \text{ Kcal/kg} \\
A &= 74.2 \log \frac{1 - e^{-0.098337}}{1 - e^{-0.02710}}
\end{align*} \]

which is in close agreement with the steam tables.

The perfect gas law gives

\[ A = RT \log \frac{\varphi_2}{\varphi_1} = 74.2 \log 2.6285 = 71.7 \text{ Kcal/kg} \]

which is in error 30.6 per cent.

7—The Adiabatic Curve

The differential equation for the adiabatic curve of the perfect vapor can be derived from Equation [6] where \( ds = 0 \). Using Equation [8], the following can be written

\[ (1/\alpha)(dx + d\varphi) = \varphi d\varphi \]

or

\[ dx = \alpha \varphi d\varphi - d\varphi \]

From Equation [13] it follows that

\[ d\varphi = c_2 \varphi^{a-1} u_{sec} d\varphi + \alpha \varphi d\varphi \]


\[ d\varphi = -\alpha \varphi d\varphi \]

Hence, making use of Equation [5], the differential equation for the adiabatic curve is

\[ d\varphi = -\alpha \varphi d\varphi \]

In Equation [44], \( \varphi \) is a function of \( T \) only, while \( u_{sec} \) is a function of \( T \) only. Thus, the integration is possible as soon as these functions are known.

Since monatomic vapors have no energy of oscillation and, for diatomic vapors, the energy of oscillation is not activated at low temperatures, in these particular cases, \( u_{sec} = 0 \). Consequently

\[ d\varphi = 0 \]

and

\[ \varphi = \text{const} \]

which can be written as

\[ p\varphi^{a-1} = \text{const} \]

in the natural properties of state.

It follows from Equation [45] that for monatomic vapors and for diatomic vapors at low temperatures each point on the curve of state in the \( \varphi, T \) diagram represents an entire adiabatic curve. Thus, all states which coincide into one point in the \( \varphi, T \) diagram are connected between each other by an adiabatic change of state.

As an approximation, the energy of oscillation of polyatomic vapors can be considered constant over limited ranges of an adiabatic change of state. Then in Equation [44] \( d\varphi \) again equals zero, and Equation [45] may be used for polyatomic vapors also.

Using the \( \alpha \) values in Equation [3], the equation of the adiabatic curve is

\[ p\varphi^{a-1} = \text{const} \]

for monatomic vapors
\[ p\varphi^{a-1} = \text{const} \]
for diatomic vapors
\[ p\varphi^{a-1} = \text{const} \]
for polyatomic vapors
Section 5, using Equations [36] and [37]. For steam, $e_0 = 136.5$ m deg C/kg$^1/2$.

Thus we have

$$\frac{p}{RT} = \frac{120 \times 10^4}{47.064 \times 763.16} = 33.410 \text{ kg/m}^2$$

and

$$\frac{T}{\theta_0} = \left( \frac{763.16}{136.5} \right)^{1/2} = 174.76 \text{ kg/m}^4$$

Equation [36] gives

$$x(z) = \frac{p/RT}{(T/\theta_0)^2} = \frac{33.410}{174.76} = 0.191176$$

From a table of the function $x(z) = \frac{1}{z_e^2}$ it is found that

$$x = 4.6933$$

From Equation [37] it follows that

$$v_1 = \frac{x}{(T/\theta_0)^2} = \frac{4.6933}{174.76} = 0.02686 \text{ m}^3/\text{kg}$$

This value agrees with 0.02687 m$^3$/kg from the V.D.I. steam table within the tolerance.

Then, from Equation [17] the enthalpy in the initial state is

$$h_1 = 4p_1 + RT\Sigma y = \frac{4 \times 120 \times 10^4 \times 0.02686}{427} + 0.11023 \times 763.2 \times 0.1613$$

which gives

$$h_1 = 315.5 + h_0 \text{ Kcal/kg}$$

where the constant $h_0$ is introduced to provide the conventional zero point of enthalpy.

To calculate the function $f(\theta/\theta_0)$, we find from the initial data

$$\theta = T^1/2 = 763.16 \times 0.02686^{1/2} = 228.58 \text{ m deg C/kg}^{1/2}$$

and

$$\theta_0 = 136.5$$

Then, the two functions constituting $f(\theta/\theta_0)$ are

$$\frac{(\theta_0/\theta)^2}{e^{(\theta_0/\theta)^2} - 1} = 0.89731$$

and

$$\log_e \frac{e^{(\theta_0/\theta)^2}}{e^{(\theta_0/\theta)^2} - 1} = 1.6513$$

Thus

$$f(\theta/\theta_0) = 1.6513 + 3 \times 0.89731 = 4.3432$$

Furthermore, from Equation [47]

$$s/R = 4.3432 + 0.2106 = 4.5538$$

The final temperature is

$$T_2 = 230 + 273.16 = 503.16 \text{ C abs}$$

For this temperature, the two terms in the function $g(T/\theta)$ are

$$\Sigma y \left( \frac{T}{\theta} \right) = 0.04518$$
For an adiabatic change of state

\[ \frac{s}{R} = \text{const} \]

Substituting the previously obtained value of \( \frac{s}{R} \), Equation [47] yields

\[ f(\theta/\theta_0) = 4.5538 - 0.05478 = 4.4990 \]

From a table of this function

\[ \theta/\theta_0 = 1.7498 \]

Hence

\[ \theta = 238.85 \text{ m deg C/kg}^{1/4} \]

and for the final volume

\[ v_1 = (\theta/T)^1 = 0.1070 \text{ m}^3/\text{kg} \]

The final pressure is obtained from Equation [38] as

\[ p_2 = 20.13 \text{ kg/cm}^2 \]

For these values \( T_2 \) and \( p_2 \), the V.D.I. steam table gives \( v_2 = 0.1071 \text{ m}^3/\text{kg} \), which agrees with our calculated value within the tolerance.

From these properties the enthalpy in the final state is obtained as

\[ h = 204.3 + h_b \text{ Kcal/kg} \]

The net adiabatic work follows from the Second Law as

\[ L = h_1 - h_2 = 111.2 \text{ Kcal/kg} \]

The V.D.I. Mollier chart gives for adiabatic expansion between the considered limits

\[ L = 112.4 \text{ Kcal/kg} \]

The deviation is within the tolerance. The example shows that the described method permits establishing a Mollier chart of satisfactory exactness.

9—Extension of the Equation of State to High Densities

The characteristic function of the perfect vapor is composed of the following four terms:

(a) Translation, according to classic theory

\[ \Psi_\text{tr} = \frac{3}{2} R \log_\theta (2\pi m k T) + R \log_\theta (v/h^3) \]

(b) Rotation, according to classic theory

\[ \Psi_\text{rot} = \left( \frac{1}{\alpha} - \frac{3}{2} \right) R \log_\theta \left( \frac{S \pi k T}{h^3} \right) + R \log_\theta \sqrt{(J K L) / \pi} \]

(c) Oscillation, according to theory of quanta

\[ \Psi_\text{osc} = R \sum_{i=1}^{\infty} \log_\theta \left( \frac{1}{1 - e^{-\theta_0 / T}} \right) \]

(d) Molecular forces, according to empirical formula Equation [38]

Equations [50] and [51] represent an empirical equation for both the liquid and the vapor state. It is evident that, in the range of high densities, the points of state do not coincide on one curve. The relations derived for the perfect vapor do not hold, but they are obtained for the limiting case \( v \gg b \).

Superimposing the curves which are represented by the two terms in Equation [51] yields \( p, v \) isothermals similar to those in van der Waals' equation of state, with the distinction that the difference between the maxima and minima approaches zero for very low temperatures as well as for very high temperatures, so that \( p \) is unable to assume negative values.

It is not possible by means of the simple assumptions of Equations [48] and [49] to obtain more than a qualitative representation of the equation of state of a liquid, because in the range of very high densities more complicated laws hold for the molecular forces.

10—Deduction of the Vapor-Pressure Curve From the Equation of State

If the equation of state of a system

\[ F(p, v, T) = 0 \]

which includes both the liquid and vapor state, known, it is possible to deduce the vapor-pressure curve

\[ f(p, T) = 0 \]

from this equation. The knowledge of such energy quantities as heat of evaporation is not necessary for the solution of this problem.

First, set up the mathematical relation, which must be satisfied by the corresponding points of state of the liquid and vapor phase. This relation is obtained by representing the system by the three properties of state which have the same value for both phases in the thermodynamic equilibrium, i.e., pressure, temperature, and thermodynamic potential. The thermodynamic potential

\[ G = u + pv - T_s \]

where \( h, J, K, L, m \) are constants. Then,

\[ \Psi = \Psi_\text{tr} + \Psi_\text{rot} + \Psi_\text{osc} + \Psi_\text{mol} \]

By differentiation according to Equation [19] the relations for the perfect vapor are obtained.

At high densities, the space occupied by the molecules has to be taken into account, whence

\[ \Psi_\text{v} = \frac{(3/2)R \log_\theta (2\pi m k T) + R \log_\theta (v - b)/h^3}{v - b} \]

Thus, Equation [19] yields the thermal equation of state

\[ p = \frac{RT}{v - b} \left( \frac{1}{v} - \frac{(\theta_0/\theta)^1/a}{e^{(\theta_0/\theta)^1/a} - 1} \right) \]

The second term represents the internal pressure resulting from the molecular forces. After rewriting this equation, for \( \alpha = 1/3 \), the following is obtained

\[ \frac{p v}{RT} = \frac{(\theta_0/\theta)^1/a}{e^{(\theta_0/\theta)^1/a} - 1} + \frac{b}{v - b} \]

and

\[ p = \frac{RTb}{v(v - b)} + \frac{R h_k^2 T c_k^2}{e^{(\theta_0/\theta)^1/a} - 1} \]

Examples [50] and [51] represent an empirical equation for both the liquid and the vapor state. It is evident that, in the range of high densities, the points of state do not coincide on one curve. The relations derived for the perfect vapor do not hold, but they are obtained for the limiting case \( v \gg b \).
may be considered as a function of the two other properties and is connected with them by the relation
\[
\left( \frac{\partial G}{\partial p} \right)_T = v \quad \ldots \ldots \ldots \ldots [54]
\]
from which
\[
G = \int \psi dp + \psi(T) \quad \ldots \ldots \ldots \ldots [55]
\]
The condition of equilibrium to be satisfied for the vapor-pressure curve is that \( G \) has the same value for both the liquid and for the vapor phases. Therefore
\[
G_l = G_v \quad \ldots \ldots \ldots \ldots [56]
\]
Since the temperature is identical in both phases, the temperature function in Equation [55], resulting from the integration of Equation [54] can be deleted in Equation [56]. Then, the condition of equilibrium can be formulated as follows. The function
\[
g = \int \psi dp
\]
has the same value in both phases; a fact which gives
\[
g_l = g_v \quad \ldots \ldots \ldots \ldots [57]
\]
and, instead of Equation [54]
\[
v = dg/dp \quad \ldots \ldots \ldots \ldots [58]
\]
Introduce this expression into Equation [52] to obtain the differential equation
\[
F \left( \frac{dg}{dp}, p, T \right) = 0 \quad \ldots \ldots \ldots \ldots [59]
\]
which when integrated at constant \( T \) gives the state of the system represented by a family of isothermals on a \( g, p \) diagram, namely
\[
\Phi(g, p, T) = 0 \quad \ldots \ldots \ldots \ldots [60]
\]
To recognize the character of the vapor-pressure curve, examine the isothermals in Equation [60] for a given equation of state. Since an analytic determination of the function in Equation [60] is not possible for the Equation of State [51], we choose as an example Berthelot’s equation of state
\[
P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \ldots \ldots \ldots \ldots [61]
\]
The constants are found from the condition that in the critical point both \( dp/dv = 0 \) and \( \partial^2 p/\partial v^2 = 0 \), namely
\[
a = (9/8)RT^2_v v_0 \quad \text{and} \quad b = (1/3)v_0 \quad \ldots \ldots \ldots [62]
\]
These results give the \( p, v \) isothermal of Fig. 10. According to Equation [58], by integration of the \( p, v \) isothermals
\[
g = \int \psi dp = pv - \int p dv
\]
which gives the \( g, v \) isothermals.

Plot \( p \) against the values of \( g \), which belong to the same \( v \), to obtain the isothermals of the \( g, p \) diagram. These isothermals represent the integral curves of Equation [60] which belong to the Differential Equation [59]. These integral curves have one double point located between two cusps. On the branch of the curve between the cusps, \( dp/\partial v > 0 \), or according to Equation [58] \( dv/dp > 0 \). This portion of the curve corresponds to the unstable space between the two phases. The double point represents the state in which the thermodynamic potentials of both phases have the same value; it is a point on the vapor-pressure curve. Thus, the two portions of the curve between the double point and the cusps represent the metastable range. The parts of the curve outside of the double point represent the ranges of stable liquid and stable vapor. Therefore, the boundary curves between the unstable and the metastable state are the loci of the cusps and the vapor-pressure curve is the locus of the double points of the family of isothermals. Thus the curves of equilibrium are represented as the curves of singularities of the integral curves in Equation [60]. The curves of singularities, however, are not singular solutions of the Differential Equation [59], because their tangents do not coincide with those of the regular integral curves, which is evident from Fig. 10.

![Fig. 10 Determination of the Phase Equilibrium From the Equation of State](image)

FIG. 10 DETERMINATION OF THE PHASE EQUILIBRIUM FROM THE EQUATION OF STATE

The problem to calculate the vapor-pressure curve for a given equation of state requires the determination of the curve of the double points in Equation [60], that is, the determination of that point of the integral curves in Equation [60], for which the condition
\[
\frac{dg}{dp} = \frac{\partial \Phi / \partial p}{\partial \Phi / \partial g} = 0 \quad \ldots \ldots \ldots \ldots [63]
\]
is satisfied by two real and different solutions. Although the graphic solution of this problem is not difficult, the analytic solution will be practicable in particular cases and then only in the implicit form of Equation [63]. To explain the method developed, first calculate the vapor-pressure curve belonging to the Equation of State [61]. By substituting Equation [58] into Equation [61], the particular form of the Differential Equation [59] is
\[
p = \frac{RT}{dp} - b - \frac{a}{T(dp/\partial p)^2}
\]
Writing
\[
w = \frac{dp}{dg} = \frac{b}{v} \quad \ldots \ldots \ldots \ldots [64]
\]
where
\[0 < w < 1\]
is obtained. Differentiation with respect to \( g \) gives

\[
\frac{dw}{dg} = \frac{\alpha}{bT} \frac{dw}{dg} \]

In this latter equation, a separation of variables is possible, so that

\[
dg = RT \frac{dw}{w(1 - w)^3} - \frac{2a}{bT} \frac{dw}{dg}
\]

and the integration gives

\[
g = RT \log \frac{\frac{\alpha}{a}}{1 - w} + \frac{\frac{\beta}{bT}}{1 - w} - \frac{2a}{bT} w + C.
\]

Let the constant of integration be zero. Now, eliminate \( w \) in Equation [66] by using the Equation of State [65]. Equation [65] then gives an equation of third degree in \( w \)

\[
w^3 - w^2 + w \left( \frac{\frac{\beta}{bT}}{a} + \frac{\frac{\alpha}{a}}{p} \right) - \frac{\beta}{bT} p = 0
\]

If the quantities

\[
\alpha = \frac{\frac{\beta}{bT}}{a} \quad \text{and} \quad \beta = \frac{\frac{\alpha}{a}}{p},
\]

are introduced

\[
w^3 - w^2 + w(\alpha + \beta) - \beta = 0.
\]

If \( w_1, w_2, w_3 \) denote the three roots in Equation [68]

\[
(w - w_1)(w - w_2)(w - w_3) = 0
\]

or

\[
w^3 - (w_1 + w_2 + w_3)w^2 + \left( w_1w_2 + w_1w_3 + w_2w_3 \right) w - w_1w_2w_3 = 0
\]

By comparison of the coefficients with Equation [68]

\[
w_1 + w_2 + w_3 = \frac{1}{\alpha}
\]

\[
w_1w_2w_3 = \frac{\beta}{\alpha}
\]

Using Equation [65], \( \beta \) can be replaced by \( \alpha \) so that

\[
\frac{\beta}{w} = \frac{\alpha}{1 - w} - \frac{\alpha}{w^2}
\]

Thus, the second of Equations [69] reads

\[
w_2 \times w_3 = \frac{\alpha}{1 - w} - w_1
\]

The roots \( w_2 \) and \( w_3 \) can be expressed by \( w_1 \) with the aid of Equations [69]. Let

\[
W = \sqrt{(1 + w)^3 - 4\alpha(1 - w)}
\]

Then by omission of the subscript of \( w_1 \)

\[
w_2 = \frac{1}{2}(1 - w + W)
\]

\[
w_3 = \frac{1}{2}(1 - w - W)
\]

Equation [68] gives \( w_1 \) according to the Cardan formula, as

\[
w = \frac{1}{3}
\]

\[
+ \sqrt[3]{\frac{1}{3} \left[ \frac{1}{2} \left( \beta \alpha + \frac{\alpha}{\beta} \right) + \left( \frac{\beta}{\alpha} - \frac{1}{3} \right) \right]}
\]

\[
+ \sqrt[3]{\frac{1}{3} \left[ \frac{1}{2} \left( \beta \alpha + \frac{\alpha}{\beta} \right) - \left( \frac{\beta}{\alpha} - \frac{1}{3} \right) \right]}
\]

Introduce the function

\[
\phi = \frac{g}{RT}
\]

which can also be considered as a function of equilibrium, because \( T \) has the same value in both phases. The three roots of \( \phi \) can be found from Equation [66] as

\[
\phi_1 = \log \frac{w}{1 - w} + \frac{1}{1 - w} - \frac{2w}{\alpha}
\]

\[
\phi_2 = \log \frac{1 - w + W}{1 - w + W} + \frac{2}{1 + w - W} - \frac{1}{\alpha} (1 - w + W)
\]

\[
\phi_3 = \log \frac{1 - w - W}{1 + w + W} + \frac{2}{1 + w + W} - \frac{1}{\alpha} (1 - w - W)
\]

Then, the complete integral function is

\[
\phi = (\phi - \phi_1)(\phi - \phi_2)(\phi - \phi_3)
\]

in which the values above are to be substituted for \( \phi_1, \phi_2, \phi_3 \). The locus of the double points of this function is the vapor-pressure curve.

Equation [74] is too complicated to calculate the curve of the double points from the condition expressed by Equation [63]. But since, in the foregoing example, the equations of each of the three branches of the equilibrium function are given, only the point of intersection of two branches need be calculated.

The problem can be solved easily by first determining which of the three roots of \( w \) belongs to the liquid, the unstable, and the vapor phase. By calculating these values for one isothermal we find that \( w_1 \) corresponds to the liquid state, \( w_2 \) to the unstable state, and \( w_3 \) to the vapor state. The same holds for the functions \( \phi_1, \phi_2, \phi_3 \). Thus, the vapor-pressure curve is the locus of the points of intersection of \( \phi_1 \) with \( \phi_2 \) on the different isothermals, so the condition is

\[
\phi_1 = \phi_3.
\]

Thus, it follows, after rewriting Equation [73] that

\[
\log \left[ \left( \frac{2}{1 + w + W} - 1 \right) \left( \frac{1 - w}{w} \right) \right] = \frac{1}{\alpha} (1 - 3w - W)
\]

\[
+ \frac{1 - w}{1 + w + W} W
\]

If, for \( w \) in Equation [76] is substituted its value from Equation [72] and the \( \alpha \) and \( \beta \) are replaced according to Equation [67] by functions of \( p \) and \( T \), Equation [53] is obtained. This is the implicit vapor-pressure curve of the Equation of State [61]. Also, \( p \) as a function of \( T \) is obtained by graphic solution of the
transcendental Equation [76] giving \( w = f(\alpha) \), as shown in Fig. 11. This curve in conjunction with Equation [70] gives

\[ \beta = \alpha \frac{w}{1 - w^2} \]

which is the curve \( \beta = f(\alpha) \) in Fig. 11. Replacing \( \alpha \) and \( \beta \) by Equation [67] gives with the aid of Equation [62]

\[ \frac{T}{T_a} = \sqrt[8]{\frac{27}{\alpha}} \quad \text{and} \quad \frac{p}{p_a} = \frac{27\beta}{T} \]

The vapor-pressure curve of Berthelot's Equation of State [61] in reduced properties can now be found from Fig. 11. The location of this curve is marked by circles in Fig. 12. The figure shows that the vapor-pressure curves of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) are very close to this curve.

**Fig. 11** Determination of the Vapor-Pressure Curve of Equation [61]

**Fig. 12** Vapor-Pressure Curve of Equation [61] Compared With Actual Substances

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**BIBLIOGRAPHY**

BIOGRAPHICAL STATEMENT

On November 23, 1903, I was born in Berlin, Germany, as son of the engineer, Ludwig Leib, formerly director with the Allgemeine Elektricitäts-Gesellschaft. From 1913 until 1922, I attended the Luisengymnasium in Berlin, and since 1923 the Institute of Technology and the University at Berlin and Munich, receiving in 1930 the degree Master in Mechanical Engineering at the Institute of Technology in Berlin. In 1931, I worked in the Research Department of the Verein Deutscher Ingenieure, and in 1932 in the Department of Heat Engineering of the A.E.G. in Berlin. From 1933 to 1937, I prepared this thesis at the Swiss Federal Institute of Technology, Zürich. I am now connected with the Combustion Engineering Company in New York, where I have been engaged in research work since 1937.