The London, Edinburgh and Dublin philosophical magazine and journal of science.
London :Taylor & Francis,[1840-1944]
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Article/Chapter Title: Saturation Specific Heats with van der Waals' and Clausius' Characteristics
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between zero and 80 alternations a second than from 80 to the frequency of light.

**Table III.**

Ratio of the Initial Values of Dielectric Constants in Steady Fields to those in Alternating Fields.

<table>
<thead>
<tr>
<th></th>
<th>$K_{80}$</th>
<th>$K_0$</th>
<th>$K_0/K_{80}$</th>
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<tbody>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td>4.6</td>
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<tr>
<td>Flint-Glass $\Delta 4.1$</td>
<td></td>
<td>8.5</td>
<td>25</td>
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<td>Resin</td>
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<td>7.0</td>
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<tr>
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<td>2.72</td>
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<td>7.0</td>
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<td>Sealing-Wax</td>
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</tbody>
</table>

**XL. Saturation Specific Heats, &c., with van der Waals’ and Clausius’ Characteristics. By Robert E. Baynes, M.A.***

[Plate VI.]

[Over twenty years ago, and shortly after reading Planck’s 1881 Memoir “Die Theorie des Sättigungsgesetzes” in vol. xiii. of Wiedemann’s Annalen, I calculated in the following manner the values for different temperatures of the latent heat of vaporization and of the saturation specific heats on the assumption of van der Waals’ equation, as also the values of other magnitudes. I did not publish my results as the equation does not represent actuality; but such of them as have not since been published by others I desire now to record, since they contrast very greatly with the results of similar calculations which I have lately made on the assumption of Clausius’ characteristic.

* Communicated by the Physical Society: read January 21, 1910.
The thermal capacities of a fluid with van der Waals' characteristic
\[(p + av^{-2})(v - b) = Rt\]
being defined by
\[dH = kdt + ldv = Kdt + Ldv,\]
their values are
\[k = \frac{Rt}{v - b}, \quad \frac{K}{R} = \frac{1}{1 - 2a(\frac{v - b}{v})^2/Rtv^3},\]
\[L = \frac{v - b}{1 - 2a(\frac{v - b}{v})^2/Rtv^3},\]
where \(k\) is in the general case a function of \(t\).
Their further calculation is simplified by using the characteristic in its 'reduced' form
\[(\pi + 3v^{-2})(3v - 1) = 8\tau,\]
in which the units employed are the critical values \(P, V, T\) of the pressure, volume, and temperature respectively, in terms of which we have
\[a = 3PV^2, \quad b = \frac{1}{3}V, \quad R = 8PV/3T;\]
and if, to simplify our calculations, we introduce * a new variable \(\mu\) defined by
\[\mu = +\sqrt{\{3v - 1\}^2 - 4\pi v^3},\]
which will be real in all the cases we need consider, and for shortness of expression put
\[A \equiv 3v - 1, \quad B \equiv \frac{1}{3}(3v - 1 - \mu), \quad C \equiv \frac{1}{3}(3v - 1 + \mu),\]
\[H \equiv \frac{1}{2}(9v - 1 + \mu), \quad D \equiv \frac{1}{2}(3v + 1 - \mu), \quad E \equiv \frac{1}{2}(3v + 1 + \mu),\]
\[F \equiv \frac{1}{2}(3 - 3v - \mu), \quad G \equiv \frac{1}{2}(3 - 3v + \mu),\]
we have
\[\pi = BC/\nu^3, \quad \tau = ADE/8\nu^3,\]
\[l/P = DE/\nu^3, \quad (K - \mu)/R = DE/FG, \quad I/V = -ADE/3FG.\]

To determine the variations of the thermal capacities we may plot their values for given values of \(\tau\) against the values of \(\pi\) or \(\nu\). We easily see that the \(l\pi, I\nu, L\nu\) curves may present singularities while the \(l\nu\) curves do not; that the value of \(K - \mu\), which is positive except when \(\nu\) lies between \(1 + \frac{1}{3}\mu\) and \(1 - \frac{1}{3}\mu\), i.e. except when \(\nu\) lies between the largest pair of the roots of the equation \(4\pi v^3 = (3\nu - 1)^2\) which are

* This variable was also employed by Ritter, *Wien. Sitz.-Ber.* July 1902.
all real when \( \tau < 1 \), is always a maximum when \( \nu = 1 \) whatever the value of \( \tau \), the maximum value for \( \tau \) being \( \frac{2\tau}{(\tau - 1)} \) and the corresponding reduced pressure being \( \frac{4\tau - 3}{3} \); that \( K - k \) has also a minimum value \( R \) when \( \nu = \frac{1}{3} \), this being also its value for any value of \( \tau \) when \( \nu = \infty \).

If the isopiestic for \( \pi \) cuts the isothermal for \( \tau \) in three points and \( \nu, \nu', \nu'' \) denote the corresponding volumes in ascending order of magnitude, then, if \( \mu \) is defined as above strictly with reference to \( \nu \),

\[
\nu'' = \nu/C, \quad \nu' = \nu/B,
\]

and the heat-capacities corresponding to \( \nu' \), expressed in terms of \( \nu \), are given by

\[
\frac{l'}{P} = \frac{ABD}{\nu^2}, \quad \frac{(K' - k)}{R} = \frac{AD}{\mu G},
\]

\[
\frac{L'}{V} = -\frac{ADE}{3\mu BG}.
\]

**Case of Saturation.**

Now, if \( \pi \) is the saturation-pressure at \( \tau \), we have also the relation

\[
3(\pi + 3/\nu')(\nu' - \nu) = 8\tau \log \left\{ (3\nu' - 1)/(3\nu - 1) \right\},
\]

so that, in the case of saturation, \( \nu \) and \( \mu \) are connected by the relation

\[
\log \left( \frac{E}{AB} \right) = 3\nu GH/AD,
\]

which may be looked upon as the equation of the liquid side of the connode or boundary curve.

[The equation of the vapour side of the connode is of the same form but with the sign of \( \mu \) changed; for we similarly obtain]

\[
\log \frac{3\nu' + 1 - \mu'}{(3\nu' - 1)(3\nu' + 1 + \mu')} = \frac{3\nu'(3 - 3\nu' - \mu')}{(3\nu' - 1)(3\nu' + 1 + \mu')(3\nu' - 1 - \mu')}
\]

if \( \mu' = + \sqrt{(3\nu' - 1)^2 - 4\pi \nu'^3} \).

From the above equation we may determine the value of \( \nu \) for any value of \( \mu \), or vice versa, and then at once obtain the corresponding values of the saturation pressure, temperature, and vapour volume \( \pi, \tau, \nu \), as well as of \( \nu'' \), so that we can easily plot the curves connecting these magnitudes with \( \mu \), or indeed with \( \nu \) or \( \tau \), &c.

We easily find that \( \mu = 0 \) for both \( \nu = 1/3 \) and \( \nu = 1 \) and that it has a maximum value \( \tau = 3065658 \), to which correspond \( \nu = 5430962, \nu' = 3:365713, \pi = 4713545, \tau = 8371466 \).
We further find, by somewhat laborious work, for the case of saturation

\[
\frac{d\pi}{dv} = BFH/Av^4, \quad \frac{dv}{dv} = -EF/\mu AB,
\]

and consequently

\[
\frac{d\pi}{d\tau} = DEF/8v^4;
\]

\[
\frac{d\pi}{d\tau} = 8BH/ADE, \quad \frac{dv}{d\tau} = -8v^4/\mu ABD.
\]

The saturation specific heats

\[\varepsilon = K + Ld\rho/dt, \quad \varepsilon' = K' + L'd\rho/dt,\]

are thus given by

\[
(\varepsilon - \kappa)/R = (DE - BH)/FG = 3v/F
\]

\[
(\kappa - \varepsilon')/R = (H - AD)/\mu G = 3v/\mu,
\]

whence also

\[
(\varepsilon - \varepsilon')/R = 3vG/\mu F.
\]

Furthermore, the latent heat of vaporization \(\lambda\) is given by

\[
\lambda/PV = (v' - v)\tau d\pi/d\tau = GH/v^2;
\]

the work of vaporization \(w\) by

\[
w/PV = \pi(v' - v) = CG/v^2;
\]

and the real latent heat \(\lambda'\) by

\[
\lambda'/PV = \lambda/PV - \pi(v' - v) = 3G/v.
\]

We may hence tabulate the values (p. 411) of, and plot curves for, all the above magnitudes with either \(v, \tau, \text{ or } \pi\) for abscissse (Pl. VI.), and we at once see that:

(i.) \(\varepsilon - \kappa\) is always positive, increasing from \(R\) to \(\infty\) as \(\tau\) increases from 0 to 1.

(ii.) \(\varepsilon' - \kappa\) is always negative and has a maximum value

\[\kappa = 4.95824\] R when \(\mu = 0.288953\), to which correspond

\[v = 4.77565, \quad v' = 6.64469, \quad \pi = 238098, \quad \tau = 724335\]; it is

\[-\infty\] when \(\tau\) is either 0 or 1.

(iii.) Inversion in the sign of \(\varepsilon'\) (which is negative for the highest and lowest temperatures) will therefore take place if

\[\kappa/R > 4.95824, \quad \text{or, on the assumption that } \kappa/R = N + \frac{1}{2}\] for an N-atomic gas, if \(N > 4.45824\), so that inversion will occur if

the gas has at least five atoms in its molecule.

In van der Waals' lately published Lehrbuch der Thermodynamik, edited by Kohnstamm, it is found by an approximate calculation that for \(\varepsilon'\) to be positive \(\kappa = 1 + R/\kappa\) must
be less than 19/17, which is equivalent to $h/R > 8.5$. Dalton
(Phil. Mag. April 1907, p. 537) has given the condition
$\kappa < 1.202$ by an interpolation method, and the foregoing
calculation gives $\kappa < 5.95824/4.95824 = 1.20168$.

(iv.) $s - s'$ is always positive and has a minimum value
$7.00789 R$ when $\mu = -262535$, which corresponds to $\nu' = 445963$
$\nu = 11.8864$, $\pi = 127530$, $\tau = 642488$.

(v.) the work of vaporization has a maximum value
$1.47215 PV \equiv 0.55206 R T$ when $\mu = 281990$ (as also found
by Ritter), to which correspond $\nu' = 467237$, $\nu = 7.80538$
$\pi = 200617$, $\tau = 700110$; it is 0 when $\tau$ is either 0 or 1.

(vi.) the greatest value of both $\lambda$ and $\lambda'$ is 9 $PV \equiv 27 RT/8$,
this occurring for $\mu = 0$, $\nu = 1.3$; $\pi = 0$, $\tau = 0$, and both decrease
continuously to the value 0 at the critical point.

Inversion of the sign of $s'$ occurs where $s' = 0$, that is,
where $3\nu/\mu = h/R$, and we can easily see, as was pointed out
by Raveau* and earlier by Duhem, that this is at the points
where the entropy along the vapour side of the connode has

critical values.

On the assumption that $h/R = N + \frac{1}{3}$ we may therefore
determine the temperatures of inversion for different values of $N$
either graphically (i.) from the diagram of the values of $(s - s')/R$
in terms of $\tau$ or (ii.) from the diagram giving the values of $\nu$, $\tau$, $\pi$
in terms of $\mu$, by finding the intersections of the lines $3\nu/\mu = N + \frac{1}{3}$
with the $\nu\mu$-curve, or thus by calculation.

If we put $n = 3(N - \frac{1}{3})/(N + \frac{1}{3})$, the desired points on the
connode correspond to $\mu = (3 - n)\nu$ and are therefore given by

$$\log \frac{(6 - n)\nu + 1}{3(\nu - 1)(n\nu - 1)} = \frac{3(3 - n)\nu(12 - n)\nu - 1}{(3\nu - 1)(n\nu + 1)(6 - n)\nu + 1},$$

and for these we have

$$\pi = (n\nu - 1)\left\{\frac{6 - n}\nu - 1\right\} / 4\nu^3$$
$$\tau = (3\nu - 1)(n\nu + 1)\left\{\frac{6 - n}\nu + 1\right\} / 32\nu^3.$$  

We also have for these points

$$\nu' = 2\nu/(3\nu - 1 - \mu) = 2\nu/(n\nu - 1), \text{ i.e. } \nu = \nu' / (n\nu' - 2),$$
or

$$\log \frac{(3\nu' - 1)(n\nu' - 2)}{(3 - n)\nu' + 2} = \frac{3\nu'(n\nu' - 3)(6 - n)\nu' + 1}{(3\nu' - 1)(n\nu' - 1)(3 - n)\nu' + 2},$$

$$\pi = (n\nu' - 2)\left\{\frac{3 - n}\nu' + 1\right\} / \nu^3$$
$$\tau = (3\nu' - 1)(n\nu' - 1)\left\{\frac{3 - n}\nu' + 2\right\} / 8\nu^3.$$  

* Journ. de Phys. 1892, p. 461.
We thus get for the points where inversion of \( s' \) occurs

<table>
<thead>
<tr>
<th>N.</th>
<th>( v' )</th>
<th>( \pi )</th>
<th>( \tau )</th>
<th>( v' )</th>
<th>( \pi )</th>
<th>( \tau )</th>
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<tbody>
<tr>
<td>5</td>
<td>2.9855</td>
<td>0.52627</td>
<td>0.85816</td>
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<tr>
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</table>

I have lately been interested to examine by this method the values of the heat-capacities, &c. of a saturated fluid in the neighbourhood of the critical point. For though v. d. Waals’ equation is not a correct representation of the behaviour of gases, yet it represents so near an approximation that its indications are of value.

If we put \( x = 1 - \gamma \), then in the neighbourhood of the critical point \( \mu \) and \( x \) are very small so that we may expand the terms in the equation of the connode in ascending powers of \( \mu \) and \( x \); we then obtain

\[
0 = \log \frac{4 - 3x + \mu}{(2 - 3x)(2 - 3x - \mu)} - \frac{3(1 - x)(3x + \mu)(8 - 9x + \mu)}{(2 - 3x)(4 - 3x - \mu)(4 - 3x + \mu)}
\]

\[
= - \frac{9}{1024} (3x + \mu)^{3/4} x - \mu + \frac{1}{5}(17x^2 - 17x\mu - 2\mu^2) + \frac{1}{4}(31x^3 - 31x^2\mu - 7x\mu^2 - \mu^3)
\]

\[
+ \frac{1}{56}(837x^4 - 837x^3\mu - 275x^2\mu^2 - 79x\mu^3 - 6\mu^4) + \ldots
\]

whence

\[
x = \mu + \frac{2}{5}\mu^2 + \frac{16}{25}\mu^3 + \frac{229}{175}\mu^4 + \ldots
\]

or

\[
\mu = x - \frac{2}{5}x^2 - \frac{8}{25}x^3 - \frac{61}{175}x^4 - \ldots,
\]

and thence we deduce

\[
\tau = 1 - \frac{1}{4}x^2 - \frac{9}{20}x^3 - \frac{129}{200}x^4 - \frac{5967}{7000}x^5 - \ldots
\]
If now we put $z^2 = 1 - \tau$, we get

$$
\mu = 2z - \frac{26}{5} z^2 + \frac{227}{25} z^3 - \frac{13544}{875} z^4 + \ldots
$$

$$
\nu = 1 - 2z + \frac{18}{5} z^2 - \frac{147}{25} z^3 + \frac{7992}{875} z^4 - \ldots
$$

$$
\nu' = 1 + 2z + \frac{18}{5} z^2 + \frac{147}{25} z^3 + \frac{7992}{875} z^4 + \ldots
$$

$$
\pi = 1 - 4z^2 + \frac{24}{5} z^4 - \frac{816}{875} z^6 + \ldots
$$

$$(s - k)/R = \frac{3}{2} z^{-1} \left( 1 - \frac{3}{5} z + \frac{31}{50} z^2 - \frac{654}{875} z^3 + \ldots \right)$$

$$(k - \nu')/R = \frac{3}{2} z^{-1} \left( 1 + \frac{3}{5} z + \frac{31}{50} z^2 + \frac{654}{875} z^3 + \ldots \right)$$

$$\lambda/\rho V = 16z(1 - \frac{23}{50} z^2 + \ldots)$$

$$\pi(\nu' - \nu) = 4z(1 - \frac{53}{50} z^2 + \ldots).$$

Thus in the neighbourhood of the critical point we may write $\pi = 4\tau - 3$ or, with greater accuracy,

$$\pi = 1 - 8(6\tau - 1)(1 - \tau),$$

and also $\lambda/RT = 6\sqrt{(1 - \tau)}$ or, with very great accuracy, $\lambda/RT = 12(27 + 23\tau)\sqrt{(1 - \tau)}$; further, the work of vaporization is one-quarter of the latent heat.

We likewise see that the mean of the saturation-densities near the critical point is $\sqrt{1(11 - \pi)}$ if $0.04(1 - \pi)^2$ is negligible, so that within this limit only the law of the straight diameter is exact with v. d. Waals' characteristic.

--

**Saturation with Clausius’ characteristic.**

With Clausius’ characteristic

$$P = \frac{Rt}{\nu - \alpha} \frac{c}{t(v + \beta)^2}$$

the critical state is given by $V = 3\alpha + 2\beta$, $p^2 = cR/216\gamma^3$, $T^2 = 8c/27\gamma R$, where $\gamma = \alpha + \beta$; and if we write $\nu = (v + \beta)/(V + \beta)$, the reduced characteristic becomes

$$\pi = \frac{8\tau - 3}{3\nu - 1}.$$
In the case of saturation we obtain from Planck’s mémoire (loc. cit.)

\[ \nu = \frac{1}{3} (r + 1 - r \cos \phi), \quad \nu' = \frac{1}{3} (r + 1 + r \cos \phi) \]

\[ \tau = \frac{3 \sqrt{3} (r + 1)^{\frac{1}{2}} r \sin \phi}{2 (r^2 \sin^2 \phi + 2r + 1)} \]

\[ \pi = \frac{6 \sqrt{3} (r^2 \sin^2 \phi - 1)}{(r + 1)^{\frac{3}{2}} (r^2 \sin^2 \phi + 2r + 1) r \sin \phi} \]

\[ \lambda/\tau = \frac{3r^2 \sin^2 \phi + 4r + 1}{(r + 1) r \sin \phi \tan \phi}, \]

where

\[ r + 1 = \frac{\cos \phi \cot^2 \phi}{\log \cot \frac{1}{2} \phi - \cos \phi}; \]

our previous mode of calculation then gives for the saturation specific heats

\[ \frac{s - \kappa}{R} \quad \text{and} \quad \frac{\kappa - s'}{R} = \frac{2 (r^2 \sin^2 \phi + 2r + 1)}{r^2 \sin^2 \phi} \times \frac{(r^2 \sin^2 \phi - 1)^2 - 3 (r + 1) \pm (2r^2 \sin^2 \phi - 1) r \cos \phi}{(r^2 \sin^2 \phi - 1) (2r + 2 - r^2 \sin^2 \phi) - 2(r + 1)}, \]

and the work of vaporization \( w \) is \( \frac{1}{4} RT \pi r \cos \phi. \)

Calculation for different values of \( \phi \) gives the following table (p. 416), whence it appears that

(i.) \( s - \kappa \) is always positive, is infinite for \( \tau = 0 \) and \( \tau = 1 \), and has a minimum value 153333 R for \( \tau = \frac{1}{83235} \):

(ii.) \( s' - \kappa \) is always negative, is \( -\infty \) for \( \tau = 0 \) and \( \tau = 1 \), and has a maximum value \(-11355 \) R for \( \tau = \frac{1}{80579} \):

(iii.) \( s - s' \) is always positive, is \( \infty \) for \( \tau = 0 \) and \( \tau = 1 \), and has a minimum value 26741 R for \( \tau = \frac{1}{81962} \):

(iv.) the latent heat \( \lambda \) increases continuously from 0 to \( \infty \) as \( \tau \) falls from 1 to 0:

(v.) the work of vaporization has a maximum value 68567 RT when \( \tau = \frac{1}{76610} \), being 0 for \( \tau = 0 \) and \( \tau = 1 \).

With this characteristic too inversion may occur in the sign of \( s' \), but now when \( \kappa < 1.088 \) or, on the former assumption that \( \kappa/R = N + \frac{1}{2} \) for an N-atomic gas, only if the gas has at least eleven atoms in its molecule.

The contrast between these conditions and the corresponding ones for v. d. Waals’ characteristic, especially in regard to \( s - \kappa \) and \( \lambda \), is very marked and is very clearly shown by the curves that have been plotted. This contrast subsists further in the neighbourhood of the critical point; for, if as before we write \( z^2 = 1 - \tau \), we find \( \tau = 1 - 7z^2 \), \( \lambda/RT = (21/\sqrt{2})z = 14.849z \), \( (s - \kappa)/R - 1.35 = 7.425/z = (\kappa - s')/R + 1.35 \), and the work of vaporization is one-seventh of the latent heat.
Clausius' characteristic.

<table>
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<th>$\phi$</th>
<th>$\psi$</th>
<th>$\pi$</th>
<th>$\pi$</th>
<th>$(s - \psi)/R.$</th>
<th>$(\psi - \psi')/R.$</th>
<th>$(s - \psi')/R.$</th>
<th>$\lambda/RT.$</th>
<th>$w/RT.$</th>
</tr>
</thead>
<tbody>
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<td>0°</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
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<td>8</td>
</tr>
<tr>
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<td>0</td>
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