X. On the isothermals of isopentane

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cury is poured off, leaving a circular film upon the upper
surface of the paper.   On unfolding the sheet, a blackish
substance is found distributed through it, graduated from the
positive towards the negative pole.

(2) If a sheet of tinfoil is included within the folds of
filter-paper, while the battery is applied, the tinfoil becomes
perforated with pin-holes.   This, however, must not be taken
per se as a proof of any direct transition of metallic mercury
through the diaphragm ; for if, instead of the mercury con-
tained in the ring, a sheet of metal is used as the upper elec-
trode, pinholes still appear in a sheet of tinfoil included in
the folds of damp filter-paper.   Moreover, if a sheet of tinfoil
is used as the upper electrode, this also becomes perforated.

(3) Again, if the sheets of tinfoil are removed, and a gold
coin is used for the upper (positive) electrode, upon the top
of the damp filter-paper, the current produces a gold discolo-
ration which penetrates the folds.   I have not yet had time
to examine this result, but it seems to throw some light upon
the formation of metallic lodes and veins.   And although the
discoloration is the effect of a steady current, and not sparks,
it may help to explain the "inductoscripts"* of Mr. F. J.
Smith.

X. *On the Isothermals of Isopentane.*
By J. ROSE-INNES, *M.A., B.Sc.*†

THE recent publication by Prof. Sydney Young of a long
    series of researches on isopentane (Proc. Phys. Soc.
Session 1894–95, pp. 602–657) offers a great opportunity to
those interested in the theory of gases.   Since isopentane is
a saturated hydrocarbon, there seems to be a reasonable hope
that we are here dealing with a substance which will not
tend to form complex molecules at low volumes, and whose
behaviour may therefore be treated as normal; and this fact,
together with the wide range of volume over which the expe-
riments have been conducted, renders Prof. Young's results
well fitted to test the various formulæ that have been from
time to time proposed.   Among these formulæ there is none
more important than that formerly suggested by Prof. Young
himself, in conjunction with Prof. Ramsay, that the pressure
of a gas kept at constant volume is a linear function of the
temperature; and the bearing of the experimental results

* "Inductoscripts," by F. J. Smith, Proc. Phys. Soc. vol. xi. p. 353
(1892).
    † Communicated by the Physical Society: read May 28, 1897.

with isopentane upon this formula is fully considered by
Prof. Young in his paper.   Accepting the formula, and
writing it as

$$p = b\mathrm{T} - a,$$

where b and a are functions of the volume only, the values of
b and a for a large number of volumes are given in the paper
(*loc. cit.* pp. 650–655), and they are sufficiently numerous to
enable us to fully test any algebraic expression that endeavours
to represent them.   I spent a considerable amount of time
examining the values of a and b, testing the formulæ that
have been proposed by various physicists, as well as others of
my own devising, without arriving at any that gave complete
satisfaction; and it occurred to me afterwards that possibly
more definite results could be secured by examining some
physical quantity which depended upon both a and b than by
examining b and a separately by themselves.   Thus if we accept
Ramsay and Young's linear law, there will be one and only
one temperature for each volume at which the gas has its
pressure equal to that given by the laws of a perfect gas.
In effect, if we put

$$p = b\mathrm{T} - a$$

as giving the actual pressure, we may also write

$$p = \frac{\mathrm{RT}}{v} + \left(b - \frac{\mathrm{R}}{v}\right)\mathrm{T} - a,$$

and this shows that $p = \dfrac{\mathrm{RT}}{v}$ if we take $\mathrm{T} = \dfrac{a}{b - \mathrm{R}/v}$.   Call
the temperature so found τ; the values of τ have been calcu-
lated and are given in the following table (p. 78); the results
above vol. 400 are not included, as they vary within such wide
limits owing to experimental errors.

In calculating this table, the value of R was taken $= \dfrac{1}{\cdot001158}$.

An examination of the table shows that the temperature in
question is very much the same for all large volumes down to
about vol. 8.   Of course the actual numbers obtained vary a
good deal, but these variations are without method, sometimes
in one direction and sometimes in another, and when the
numbers are plotted against $v^{-\frac{1}{3}}$ it appears to me impossible
to tell from an inspection of the diagram whether the value
above vol. 8 is on the whole increasing or decreasing.   These
variations may therefore be attributed to experimental error;
and they may be to a large extent got rid of by employing
" smoothed " values of b and a, as was done in Ramsay and

Volume.	τ.	Volume.	τ.	Volume.	τ.
350......	851·9	22......	835·8	4·3 ...	804·6
300......	835·4	20......	845·9	4·0 ...	799·1
260......	820·8	19......	854·7	3·8 ...	792·3
230.. ...	825·6	18.....	848·7	3·6 ...	777·3
200......	969·6	17......	850·9	3·4 ...	764·0
180......	935·6	16......	845·3	3·2 ...	737·2
160......	846·7	15......	854·1	3·0 ...	715·5
140......	787·0	14......	848·9	2·9 ...	696·5
120......	808·9	13......	847·8	2·8 ...	675·9
100......	804·1	12......	844·1	2·7 ...	656·4
90......	793·8	11......	840·1	2·6 ...	637·7
80......	773·4	10......	843·5	2·5 ...	615·2
70......	854·7	9·5 ...	846·7	2·4 ...	593·7
60......	876·2	9......	838·3	2·3 ...	565·9
50......	871·6	8·5 ...	834·5	2·2 ...	541·1
45......	853·1	8......	833·7	2·1 ...	511·2
40......	816·2	7·5 ..	833·2	2·0 ...	478·7
36......	832·8	7.....	832·2	1·9 ...	446·3
33......	820·0	6·5 ...	828·1	1·8 ...	408·6
30......	833·7	6......	827·2	1·7	367·2
28	835·1	5·5 ...	819·8	1·6 ...	318·4
26......	846·7	5......	813·7		
24......	848·0	4·6 ...	809·5		

Young's paper on ether (Phil. Mag. xxiii. p. 441). Prof. Young has not given any smoothed values of b for isopentane, however, and I have thought it better not to use my own smoothed values, so as to employ numbers that are above the suspicion of bias towards any particular theory.

The mean value of τ for all volumes above 8 is 842·4; and this number could be taken as the true value for all such volumes without introducing any serious error. Below vol. 8, however, the value of τ distinctly diminishes with the volume; and by the time the critical point is reached, τ is not more than about 804. It is not easy to find a formula for τ which will give the experimental results throughout the whole range of volume; but whatever may turn out to be its proper algebraic expression, there appears to be little doubt that its initial decrease from the maximum value varies as a higher power of the density than the first.

The result appears to me to be of importance, since it is by itself sufficient to reveal the inadequacy for isopentane of many of the gas-formulæ that have been proposed. We have seen that

$$\tau = \frac{av}{bv - \mathrm{R}}.$$

Suppose that we can put

$$b = \frac{R}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + \text{ higher powers of } \frac{1}{v},$$

$$a = \frac{A_2}{v^2} + \frac{A_3}{v^3} + \text{ higher powers of } \frac{1}{v} ;$$

Then

$$\tau = \frac{A_2 + A_3 v^{-1} + \ldots}{B_2 + B_3 v^{-1} + \ldots},$$

$$= \frac{A_2}{B_2} + \frac{A_3 B_2 - A_2 B_3}{B_2^2} v^{-1} + \text{higher powers of } \frac{1}{v}.$$

If b and a in any gas-formula can be expanded in powers of v^{-1} as assumed, and if $A_3 B_2 - A_2 B_3$ is different from zero, which will in general happen, the decrease of τ from the maximum value will be as v^{-1}; so that the proposed formula is inadmissible.

Let us now return to the quantities a and b. The values of $\frac{1}{av^2}$ were plotted against $v^{-\frac{1}{3}}$ by Prof. Young, and the resulting diagram is given in his paper (*loc. cit.* p. 653). The curve determined by the points plotted would seem to be of a somewhat complicated character, and I do not think it possible to obtain any simple formula that will reproduce it entirely. On the other hand, there seems to be considerable evidence of discontinuity in the neighbourhood of vol. 3·4; and even if there is not discontinuity in the true mathematical sense of the word, there appears to be such a rapid alteration of behaviour as to amount in practice to the same thing. The easiest plan is to treat the curve as consisting of two parts, the formula passing abruptly from one expression to another somewhere in the neighbourhood of vol. 3·4. Whether this accurately represents what takes place in nature is uncertain, but there is no doubt that it immensely simplifies the problem. We may therefore confine our attention to volumes above 3·4; and of the formulæ already proposed I found the best to be that suggested by Mr. W. Sutherland, who has given a gas-formula equivalent to putting

$$a = \frac{l}{v(v + k)},$$

where l and k are two constants characteristic of the gas (Phil. Mag. xxxv. p. 215). I have taken the following values of the constants

$$l = 5{,}420{,}800, \qquad k = 3·636.$$

The next step was to find a formula for b.   Now

$$b = \frac{R}{v} + \frac{a}{\tau},$$

and the conditions already discovered with respect to the algebraic expression for τ considerably restrict the field of research; this is an advantage, as it lessens the amount of arithmetical work to be performed.   I found that fairly good results could be obtained by putting

$$b = \frac{R}{v}\left(1 + \frac{e}{v + k - \dfrac{g}{v^2}}\right),$$

where R and k have the values already given and

$$e = 7\cdot473, \qquad g = 6\cdot2318.$$

By combining the formulæ given above for a and for b, we obtain as the formula for the isothermals

$$p = \frac{RT}{v}\left(1 + \frac{e}{v + k - \dfrac{g}{v^2}}\right) - \frac{l}{v + k},$$

where R, e, k, g, and l are constants, and have the values already given.

In order to test this formula it is desirable to draw a system of isothermals, but if this be done in the ordinary Andrews' diagram the result is not satisfactory, as the range of p is so large.   It was found possible to obtain a good diagram, however, by calculating pv and plotting it against $v^{-\frac{1}{3}}$; the calculated isothermals are shown as continuous lines, while the experimental values are put in as dots.   It will be seen that there is a fair agreement between calculation and experiment down to about vol. 3·4.   Below this volume there is no longer any agreement; we should naturally expect such a result, since the formula for a admittedly holds up to the neighbourhood of vol. 3·4 only.   Therefore, even if the calculated isothermal were to agree with the found isothermal below vol. 3·4 for some one temperature, this would only happen by a compensation of errors, and could not occur for any second temperature.

It will be noticed that in the neighbourhood of vol. 16 there is a sensible divergence between the calculated and found isothermals amounting to slightly over 1 per cent. This divergence is certainly unsatisfactory as far as it goes;

but differences just as great have occurred in the past in inquiries of this kind between the results of independent observers experimenting on the same substance. For the present, then, and pending the confirmation of Prof. Young's results by some other observer, we may take the simple formula given above as representing all that we certainly know concerning the behaviour of isopentane under the conditions of volume specified.

The formula proposed may be employed to calculate the critical constants ; this may be done by a method depending solely on Ramsay and Young's linear law. Let us take the equation

$$p = b\mathrm{T} - a,$$

and differentiate it with respect to v, keeping T constant,

$$\frac{dp}{dv} = \mathrm{T}\frac{db}{dv} - \frac{da}{dv}.$$

Differentiate again

$$\frac{d^2p}{dv^2} = \mathrm{T}\frac{d^2b}{dv^2} - \frac{d^2a}{dv^2}.$$

At the critical point $\dfrac{dp}{dv}$ and $\dfrac{d^2p}{dv^2}$ vanish together, so we have

$$\mathrm{T}\frac{db}{dv} - \frac{da}{dv} = 0,$$

$$\mathrm{T}\frac{d^2b}{dv^2} - \frac{d^2a}{dv^2} = 0.$$

Eliminating T this gives

$$\frac{db}{dv}\frac{d^2a}{dv^2} - \frac{d^2b}{dv^2}\frac{da}{dv} = 0.$$

When v has been calculated from this equation we may obtain T by putting

$$\mathrm{T} = \frac{da}{dv} \div \frac{db}{dv},$$

and when v and T are known the original isothermal equation will give p.

In this way we may obtain the following results :—

$$\left\{\begin{array}{l} \text{critical volume} = 4\cdot5, \\ \text{critical temperature} = 191^\circ\cdot7 \text{ C.,} \\ \text{critical pressure} = 26250, \end{array}\right.$$

which agree fairly well with the numbers found experimentally by Prof. Young.

There is one of the isothermals in the set determined by our formula which is of peculiar interest. The biggest value of τ occurs when v is indefinitely large, its value being then $\dfrac{l}{\mathrm{R}e}$. Let us call this quantity τ_0 for shortness, and let us see what form the isothermal for this particular temperature takes. We shall easily obtain

$$p = \frac{\mathrm{R}\tau_0}{v} + \frac{lg}{v^3\left(v + k - \dfrac{g}{v^2}\right)(v + k)},$$

so that the pressure for a long range of volume is practically given by Boyle's law; and when an increase does occur, it varies as the *fifth* power of the density. In the case of isopentane this is merely a deduction from theory, since the temperature required is 567° C. ; much too high to allow of any experiments being carried out for verification. Indeed, for most other substances, the temperature of minimum deviation from Boyle's law, being much higher than the critical temperature, is much too high to allow of any experiments being performed there. An exception may be made, however, in the case of nitrogen, which has a very low critical temperature. The following are the values of pv at 16° C. for nitrogen under different pressures determined by M. Amagat ("Mémoires sur l'élasticité et la dilatabilité des Fluides jusqu'aux très-hautes Pressions," *Ann. Chim. Phys.* 6th series, vol. xxix. p. 107).

Pressure in metres of mercury.	pv.	Pressure in metres of mercury.	pv.
·76	1·0000	45	·9895
20	·9930	50	·9897
25	·9919	55	·9902
30	·9908	60	·9908
35	·9899	65	·9913
40	·9896		

From this table it is evident that at 16° C. for nitrogen we are only a short way off the temperature of minimum deviation from Boyle's law. At temperatures higher than the temperature of minimum deviation the gas would have pv increasing with pressure from the first, and this is what happens with hydrogen at ordinary temperatures.