

On the Law of Cailletet and Mathias and the Critical Density

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solution of NaCl places it outside the class of simple mixtures considered in what precedes.

The result of this investigation may be summed up as follows:—

(1) No one of the three theoretical formulæ (1), (2), (3) represents the viscosity of a mixture with sufficient closeness.

(2) The empirical formula $\left(\frac{1}{\eta}\right)^m = v_1 \left(\frac{1}{\eta_1}\right)^m + v_2 \left(\frac{1}{\eta_2}\right)^m$ with a suitable value for m gives a satisfactory representation.

(3) It leads also to Slotte's formula for the variation of viscosity of a liquid with temperature.

XXX. *On the Law of Cailletet and Mathias and the Critical Density.* By SYDNEY YOUNG, D.Sc., F.R.S., University College, Bristol*.

IN a very interesting paper (*Mém. de la Soc. Roy. des Sci. de Liège*, sér. 3, ii. 1899) M. E. Mathias discusses the law of the Rectilinear Diameter, discovered in 1886 by M. Cailletet and himself, and the law of the corresponding states of matter. The law of Cailletet and Mathias may be stated simply in this way:—The means of the densities of liquid and saturated vapour for any stable substance are a rectilinear function of the temperature.

It has been shown (Mathias, *Ann. de la Fac. des Sci. de Toulouse*, 1892; Young, *Phil. Mag.* Dec. 1892, p. 506) that if the generalizations of van der Waals regarding corresponding temperatures, pressures, and volumes are correct, the angular coefficient α [$D_t = D_0 + \alpha t$, where D_t and D_0 are the means of the densities at t° and 0° respectively] of the diameters of different substances should be directly proportional to their critical densities, and inversely proportional to their absolute critical temperatures; or that for any substance

$$\alpha = \text{const.} \times \frac{D_c}{T_c};$$

* Read June 22, 1900.

thus

$$\frac{\alpha T_c}{D_c} = \text{const.} = \alpha.$$

M. Mathias points out that in order to test the truth of the law of corresponding states, it is only necessary to ascertain whether α is really a constant. He then discusses the conditions necessary for the determination of α .

For a certain number of substances the critical temperature and the densities of liquid and saturated vapour from about the ordinary boiling-point to the critical point have been determined; and in these cases there is no difficulty. From the mean densities at a series of temperatures α is found, and D_c is then calculated from the formula

$$D_c = D_0 + \alpha (T_c - 273).$$

In the great majority of cases, however, the only density determinations that have been made are those of the liquid below the boiling-point. We may, however, calculate the densities of saturated vapour at these low temperatures if the vapour-pressures are known, on the assumption that the vapour-density is practically normal; and thus the mean densities of liquid and saturated vapour may be ascertained.

Now the law of Cailletet and Mathias has been found to hold good for a considerable number of substances from the boiling-point to the critical point; and M. Mathias, making the very natural assumption that the law may be relied upon at lower temperatures, calculates the value of α from the mean densities below the boiling-point. If the critical temperature is known, the critical density is then calculated as before; but for most substances the critical temperature has not been directly determined; and M. Mathias discusses the methods, notably that of Thorpe and Rücker, that have been suggested for calculating this constant.

M. Mathias shows that if, in Thorpe and Rücker's formula

$$T_c = \frac{T_2 d_1 - T_1 d_2}{A(d_1 - d_2)},$$

$A = 2$, then it follows that $\alpha = 1$.

He further shows how, if $\alpha = 1$, it would be possible to ascertain both the critical density and the critical temperature by a geometrical method. In most cases, however, A differs

sensibly from 2 and α from unity, and the geometrical method is then inapplicable; neither can the critical temperature be calculated with sufficient accuracy by employing the value of A , 1.995, adopted by Thorpe and Rücker.

It occurred to me that A , though not quite the same for different substances, might possibly be related to the composition in some simple way; and I have therefore calculated its value (taking 0° and the boiling-point under normal pressure as the two temperatures) for the thirty compounds referred to in this paper; these constants are given in Table I. Unfortunately there does not seem to be a sufficiently marked connexion between the values of A and the composition to be of much practical use.

M. Mathias arrives at the conclusion—which, I think (except for a few special cases), is quite justified—that it is necessary to make a direct determination of the critical temperature.

M. Mathias then proceeds to the examination of experimental data derived from various sources. The critical temperature, the vapour-pressures, and the densities of liquid chlorine have been very carefully determined by Knietsch; and M. Mathias has calculated the densities of the saturated vapour below the boiling-point ($-33^\circ.6$), and finds that the constancy of both α and D_c are apparently extremely satisfactory; but the value of α (.7675) is very far from unity. The value of D_c is .5782; but it may be pointed out that the ratio of this to the theoretical density at the critical temperature and pressure as observed by Knietsch is only 3.03, a very low number.

Among the other substances examined by M. Mathias is normal decane, for which the densities of liquid have been determined only at low temperatures. In this case the values of α , a , and D_c seem to be at variance with those obtained by myself for the lower normal paraffins, as will be seen from the table below:

	α .	a .	D_c .
Pentane000460	0.931	.2324
Hexane.....	.000446	0.967	.2343
Heptane000440	1.013	.2344
Octane000440	1.075	.2330
Decane.....	.000380	0.928	.2471

For the four lower paraffins α and D_c show very slight variations, whilst a rises considerably with increase of molecular weight, so that the values calculated for decane appear improbable.

In view of these apparently abnormal results it seemed advisable to undertake a careful examination of the whole of the data which I have obtained for thirty substances. In all cases except the alcohols the critical densities were calculated by the method of Cailletet and Mathias, the mean densities above the boiling-points only having been used except for one or two substances; and though the deviations from the formula $D_t = D_0 + \alpha t$ differ somewhat considerably, there did not appear to be any definite tendency to curvature except possibly in a few cases. I have, indeed, attributed these deviations to errors of experiment; and this view was strengthened by the fact that for normal pentane, with which very careful determinations were made from 0° to within $0^\circ.05$ of the critical temperature, the deviations were exceedingly small and well within the limits of experimental error.

As will be seen later, however, it turns out that in choosing normal pentane for this special investigation I happen to have hit on the one substance which does not show the slightest deviation from the law of Cailletet and Mathias.

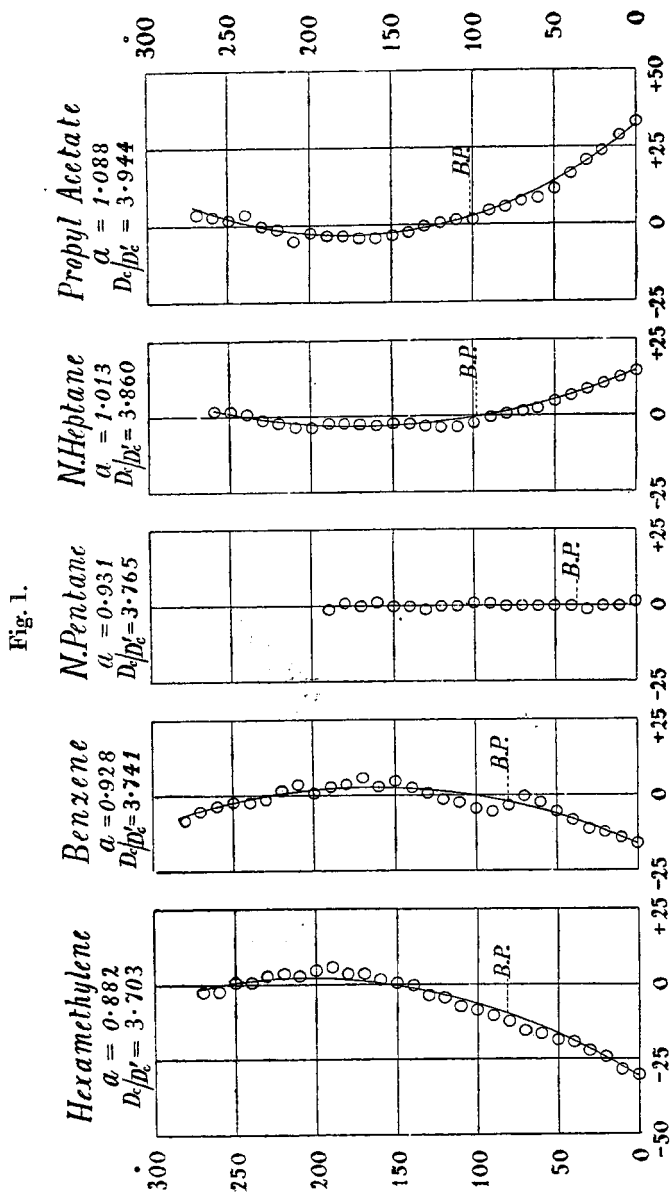
Since the publication of M. Mathias's paper I have calculated the mean densities of all thirty substances at intervals of ten degrees between 0° and the boiling-point; and it became evident that for many of them the deviations increased rapidly below the boiling-point. Moreover, on plotting all the differences between the mean densities and those calculated from the formula $D_t = D_0 + \alpha t$ against the temperature, distinct curvature was noticeable in many cases. This will be seen from the curves (fig. 1) for hexamethylene, benzene, normal heptane, and propyl acetate.

The drawn curves are calculated from the formula

$$D_t = D_0 + \alpha t + \beta t^2,$$

α being negative in these and all other cases (for both formulæ), whilst β is positive in the first two cases but negative in the last two.

For normal pentane it will be seen that there is absolutely no indication of curvature, so that $\beta=0$; for the alcohols,



on the other hand, the curvature (in the same direction as that for propyl acetate) is so pronounced that a fourth term,

γt^3 , has to be introduced into the formula to reproduce the data.

The values of a and of $\frac{D_c}{D'_c}$ [the ratio of the actual to the theoretical density at the critical point] are given for the five substances; those for methyl alcohol are very high, 1.142 and 4.521 respectively.

It is remarkable that as the curvature changes in such a manner that β passes from a positive value, through zero, to a negative value, a and $\frac{D_c}{D'_c}$ regularly increase. It is especially remarkable that for normal pentane, for which $\beta=0$, the value of $\frac{D_c}{D'_c}$ (3.765) is almost exactly that which may be taken as normal for substances whose molecules undergo no dissociation or polymerization. (The ratio given by van der Waals is $\frac{8}{3}=2.6$, but, as shown by Guye and by Heilborn, if we accept O. E. Meyer's correction for the relation between b in the formula of van der Waals and the space actually occupied by the molecules, this number should be multiplied by $\sqrt{2}$, which would give 3.77.)

That being so, we may perhaps take the normal value of a to be about 0.93.

It seems unnecessary to give the differences of the observed mean densities from those calculated from the formula $D_t = D_0 + \alpha t$ at intervals of ten degrees for each of the thirty substances, but in Table I. I have given the values of D_0 , $\alpha \times 10^6$, a , $\frac{D_c}{D'_c}$, $\frac{D_c}{D'_c} - 3.770$, the difference between the observed and calculated mean density at 0° , and lastly A (Thorpe and Rücker).

The substances are arranged in ascending order of $\frac{D_c}{D'_c}$, and it will be noticed that there is, on the whole, a distinct tendency for a to rise; thus the values of a on the one side of normal pentane are, with one exception (stannic chloride), lower than .931, and those on the other side are, again with one exception (fluorbenzene), higher.

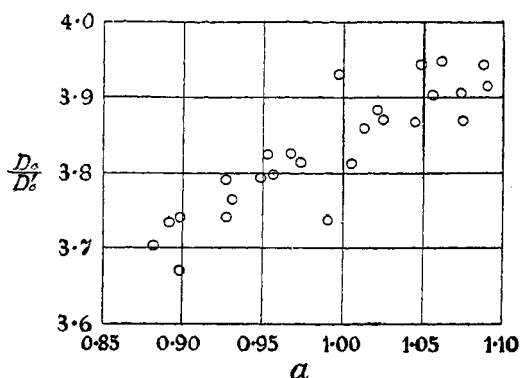
Again, all the differences at 0° on the one side of normal pentane are negative, and with one exception (fluorbenzene) all on the other side are positive.

TABLE I.

Name.	D ₀ .	$a \times 10^6$.	$\frac{T_c}{a} = \frac{T_c}{D_c}$.	Error in Mean density at 0°. Calc. — Obs.	$\frac{D_c}{D_c'}$.	$\frac{D_c}{D_c'} - 3.770$.	A (Thorpe and Rucker).
Carbon Tetrachloride8117	— 900	0.899	— 47	3.670	— 0.100	1.996
Hexamethylene.....	.3954	— 436	0.882	— 30	3.703	— 0.067	2.006
Isopentane.....	.3197	— 454	0.892	— 5	3.734	— 0.036	1.984
Stannic Chloride	1.1356	— 1240	0.991	— 38	3.738	— 0.032	1.934
Benzene.....	.4485	— 502	0.928	— 16	3.741	— 0.029	1.986
Di-isopropyl.....	.3595	— 433	0.899	— 4	3.741	— 0.029	2.022
Normal Pentane3251	— 460	0.931	— 0	3.765	— 0.005	1.994
Fluorobenzene.....	.5224	— 587	0.927	— 9	3.791	+ 0.021	2.030
Chlorobenzene.....	.5650	— 550	0.949	+ 11	3.794	+ 0.024	2.030
Iodobenzene9318	— 775	0.956	+ 15	3.798	+ 0.028	(2.030)
Di-isobutyl3567	— 433	1.005	+ 17	3.813	+ 0.043	1.978
Ether.....	.3687	— 547	0.974	+ 2	3.814	+ 0.044	1.937
Bromobenzene7634	— 694	0.953	+ 25	3.825	+ 0.055	(2.030)
Normal Hexane3390	— 446	0.967	+ 4	3.827	+ 0.057	1.982
Normal Heptane3518	— 440	1.013	+ 15	3.860	+ 0.090	1.980
Methyl Isobutyrate4577	— 583	1.045	+ 20	3.868	+ 0.098	1.956
Normal Octane3634	— 440	1.075	+ 42	3.870	+ 0.100	1.959
Propyl Formate4658	— 590	1.025	+ 14	3.871	+ 0.101	1.967
Ethyl Formate4759	— 649	1.021	+ 17	3.885	+ 0.115	1.959
Methyl Propionate4721	— 621	1.055	+ 27	3.903	+ 0.133	1.960
Methyl Butyrate4640	— 582	1.074	+ 39	3.907	+ 0.137	1.956
Ethyl Propionate4587	— 593	1.074	+ 25	3.917	+ 0.147	1.926
Methyl Formate5025	— 715	0.997	+ 6	3.932	+ 0.162	1.982
Propyl Acetate4585	— 587	1.088	+ 34	3.944	+ 0.174	1.943
Methyl Acetate4830	— 674	1.049	+ 32	3.945	+ 0.175	1.975
Ethyl Acetate4644	— 625	1.061	+ 22	3.949	+ 0.179	1.940
Ethyl Alcohol4138	— 556	1.043 *	+ 107	4.016 *	+ 0.246	2.280
Propyl Alcohol4184	— 528	1.030 *	+ 88	4.021 *	+ 0.251	2.277
Methyl Alcohol.....	.4190	— 602	1.142 *	+ 139	4.521 *	+ 0.751	2.255
Acetic Acid5399	— 587	0.994	+ 50	4.993	+ 1.223	2.077

That there is a relationship of the values of α to the ratios $\frac{D_c}{D'_c}$ is clearly seen by the diagram (fig. 2).

Fig. 2.



With regard to the differences at 0° , M. Mathias notices (*loc. cit.* p. 19) that at low temperatures the substituted ammonias give values of α that increase as the temperature falls, but he regards this as being due to the approach to the solidifying-point.

It appeared to me more probable, however, that in most cases the mean densities would be more accurately represented by the equation

$$D_t = D_0 + \alpha t + \beta t^2$$

than by the simpler one $D_t = D_0 + \alpha t$, and I therefore calculated the constants D_0 , α , and β for all the substances. For the alcohols, however, it was necessary to introduce a fourth term, γt^3 , to get a satisfactory agreement.

I am indebted to Miss E. C. Fortey, B.Sc., for much valuable assistance with these calculations.

The constants are given in Table II., and here it will be seen that whilst the values of α are without exception negative, those of β on the one side of normal pentane are all positive, and, with three exceptions, those on the other side are negative. These exceptions are: fluorobenzene, which was before found to behave abnormally; hexane, for which $\beta=0$; and methyl alcohol, for which γ has a very high negative value.

The relationship of β to $\frac{D_c}{D'_c}$ is well seen by the diagram (fig. 3).

Fig. 3.

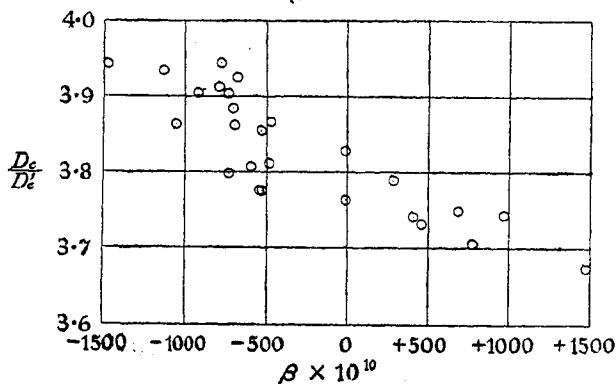


TABLE II.

Name.	D_0 .	$\alpha \times 10^7$.	$\beta \times 10^{10}$.	$\gamma \times 10^{13}$.
Carbon Tetrachloride	8165	- 9564	+ 1480	
Hexamethylene	3985	- 4685	+ 791	
Isopentane	3202	- 4658	+ 463	
Stannic Chloride	11387	- 12760	+ 977	
Benzene	4501	- 5248	+ 693	
Di-isopropyl	3401	- 4445	+ 413	
Normal Pentane	3232	- 4610	0	
Fluorbenzene	5236	- 6000	+ 293	
Chlorobenzene	5640	- 5337	- 509	
Iodobenzene	9303	- 7556	- 519	
Di-isobutyl	3550	- 4115	- 592	
Ether	3685	- 5377	- 475	
Bromobenzene	7609	- 6655	- 725	
Normal Hexane	3388	- 4445	0	
Normal Heptane	3504	- 4192	- 621	
Methyl Isobutyrate	4558	- 5593	- 689	
Normal Octane	3590	- 3954	- 1046	
Propyl Formate	4647	- 5748	- 459	
Ethyl Formate	4741	- 6251	- 694	
Methyl Propionate	4696	- 5921	- 729	
Methyl Butyrate	4601	- 5430	- 906	
Ethyl Propionate	4564	- 5644	- 784	
Methyl Formate	5020	- 7013	- 665	
Propyl Acetate	4553	- 5469	- 1124	
Methyl Acetate	4799	- 6280	- 1467	
Ethyl Acetate	4624	- 5992	- 764	
Ethyl Alcohol	4028	- 3827	- 5940	+ 651
Propyl Alcohol	4095	- 3790	- 3750	- 5533
Methyl Alcohol	4050	- 4479	+ 1330	- 23760
Acetic Acid	5355	- 5366	- 1191	

A comparison of the results by the two formulæ is given in Table III. Under $\frac{\Delta}{n}$ are given the mean differences multiplied by 10^4 between the observed and calculated densities without regard to sign; under $\frac{\Delta'}{n}$, the algebraical sum of the differences multiplied by 10^4 and divided by the number of observations.

The numbers under I. refer to the formula with two constants, those under II. to the formula with three constants (four for the alcohols).

Taking the whole range of temperature for each substance, it will be seen that the agreement when the three constants formula is used is very much better than when the simpler one is employed. Excluding the alcohols and acetic acid, the molecules of which are almost certainly of different complexity in the gaseous and liquid states, the mean value of $\frac{\Delta}{n}$ for the 26 substances is 5.40 for the formula with two constants as against 1.51 for that with three. That $\frac{\Delta'}{n}$ is very small in each case for the formula with three constants, not only for the whole range of temperature but also for the temperatures above and below the boiling-point taken separately, may be regarded as evidence that the curves represent the results with satisfactory accuracy; and, if that is so, the values of $\frac{\Delta}{n}$ for the same formula may be taken as a measure of the experimental errors which, it will be seen, differ considerably for different substances. The large errors in the case of stannic chloride may be explained by the fact that this compound attacks mercury at all temperatures whilst carbon tetrachloride does so at high temperatures, so that special experimental methods had to be devised. Again, the observations with iodobenzene had to be made by artificial light as the substance becomes rapidly coloured on exposure to daylight. Acetic acid gave a good deal of trouble at the highest temperatures, owing to repeated bursting of the tubes, but the comparatively large errors with ether and ethyl and propyl alcohol are not easily accounted for.

TABLE III.

Name.	$\frac{\Delta}{n}$		$\frac{\Delta'}{n}$			
	Whole Range.		Above B.-P.		Whole Range.	
	I.	II.	I.	II.	I.	II.
Carbon Tetrachloride	1200	254	415	305	-	-004
Hexamethylene.....	907	129	368	147	-	+007
Isopentane	195	068	150	069	+	-026
Stannic Chloride	917	325	518	429	+	676
Benzene.....	469	134	325	150	-	248
Di-isopropyl.....	257	109	206	106	-	030
Normal Pentane	070	040	062	037	+	010
Fluorobenzene	472	224	221	210	-	148
Chlorobenzene	332	131	214	107	+	039
Iodobenzene	429	250	255	356	+	186
Di-isobutyl	393	093	088	118	+	321
Ether	390	345	456	406	-	130
Bromobenzene	652	163	245	245	+	489
Normal Hexane	125	121	124	106	+	025
Normal Heptane	381	074	218	082	+	144
Methyl Isobutyrate	478	178	224	229	+	337
Normal Octane	1083	100	229	129	+	930
Propyl Formate	289	141	139	139	+	156
Ethyl Formate	546	108	306	111	+	329
Methyl Propionate	712	169	328	162	+	015
Methyl Butyrate	1014	117	267	150	+	855
Ethyl Propionate.....	514	168	144	167	+	364
Methyl Formate	200	136	178	155	+	064
Propyl Acetate.....	754	104	253	100	+	561
Methyl Acetate.....	762	142	300	167	+	479
Ethyl Acetate	492	092	165	071	+	412
Ethyl Alcohol	2940	428	1459	518	-	052
Propyl Alcohol.....	2611	422	2000	535	+	530
Methyl Alcohol	4532	242	2639	294	+	1588
Acetic Acid	1106	413	690	395	+	463
Mean, excluding Alcohols and Acetic Acid	540	151	246	171	±	343
						±014
						±1054
						±043
						±061
						±030
						±071
						±194
						±129
						±088
						±125
						±062
						±071
						±039
						±006
						±011
						±017
						±061
						±039
						±044
						±033
						±029
						±078
						±059
						±035
						±129
						±194
						±071
						±115
						±030

It remains to be seen whether the simpler formula $D_t = D_0 + \alpha t$ is sufficiently accurate to be employed for temperatures between the boiling-point and the critical-point. The values of $\frac{\Delta}{n}$ and $\frac{\Delta'}{n}$ above the boiling-point are therefore given in the table, and it will be seen that the improvement effected by introducing the third constant is very much smaller than for the whole range of temperature. Thus the mean value of $\frac{\Delta}{n}$ falls only from 2.46 to 1.71, as against 5.40 to 1.51 for the whole temperature range, and for $\frac{\Delta'}{n}$ the fall is only from 0.64 to 0.30 as against 3.43 to 0.14.

There is therefore for this range of temperature, except in the more extreme cases (near the top and bottom of the table), not very much to choose between the two formulæ.

On the other hand, a comparison of the values of $\frac{\Delta'}{n}$ for the two formulæ below the boiling-point brings out the difference between them in a most striking manner. For the formulæ with two constants the first eight values are negative, and the rest with one exception (ether, for which the experimental errors are large and the temperature range small) are positive, and, omitting the alcohols, they range from -31.62 to $+22.36$, or, including the alcohols, to $+94.00$. For the formula with three constants the $+$ and $-$ signs are fairly evenly distributed, and, excluding the alcohols and acetic acid, the extreme values are -0.90 and $+1.00$. Again, for the simpler formula, the mean value of $\frac{\Delta'}{n}$, excluding the alcohols and acetic acid, is ± 10.54 , but for the formula with three constants it is only ± 0.43 . It is quite clear from this that the constants for the formula $D_t = D_0 + \alpha t$ calculated exclusively from the densities at temperatures below the boiling-point would in many cases differ very considerably from those calculated from the densities at temperatures above the boiling-point; and that the differences between the calculated critical densities $\{D_c = D_0 + \alpha(T_c - 273)\}$ and also between the values of α in the two cases might also be considerable.

Thus for normal octane the numbers would be

	D_0	α	D_c	α
Below the boiling-point...	·3592	·000409	·2381	0·978
Above the boiling-point...	·3634	·000440	·2330	1·075

The constants calculated from the densities below the boiling-point approach fairly close to those obtained by M. Mathias for normal decane from the densities between 0° and 100° (p. 482) though, as might be expected from the higher molecular weight of decane and from the fact that the densities were not taken even to the boiling-point, the errors in that case are still greater.

There seems to be no doubt that, in order to find the critical density with the greatest possible accuracy, it would be best to make use of the whole of the available data and to employ the formula with three constants, thus

$$D_c = D_0 + \alpha(T_c - 273) + \beta(T_c - 273)^2.$$

This has been done for the thirty substances, and the new and old critical densities, also the new values of $\frac{D_c}{D'_c}$, are given in Table IV.

For convenience of reference the critical temperatures and pressures, the specific gravities at 0°, and the boiling-points under normal pressure are also given in the table. The order is in ascending order of the recalculated values of $\frac{D_c}{D'_c}$.

It will be seen that the differences between the new and old critical densities are quite small. They are greatest for chlorobenzene, bromobenzene, and iodobenzene; but the critical temperatures of these compounds are very high, and the density determinations have only been taken to 260° or 270°. The greatest difference, that for iodobenzene, amounts to 0·55 per cent., and for this substance there is an extrapolation through 180°.

In the case of the alcohols the differences are not excessive because the old values were not obtained from the simple formula but graphically from curves drawn through the points representing the mean densities.

Of the remaining 26 substances benzene shows the greatest

TABLE IV.

Name.	Sp. Gr. at 0°.	B.P. at 760 mm.	Critical Temperature.	Critical Pressure.	Critical Density.		De D _c Corrected.
					Old.	Corrected.	
Carbon Tetrachloride	1.63255	76.75	283.15	millim.	5569	5576	3.674
Hexamethylene	79675	80.9	280.0	34180	2733	2735	3.706
Isopentane	63930	27.45	187.8	30250	2344	2345	3.732
Di-isopropyl	67948	58.1	227.4	23020	2410	2411	3.742
Stannic Chloride	227875	114.1	318.7	28080	7404	7419	3.744
Benzene	90006	80.2	288.5	36595	3037	3045	3.750
Normal Pentane	64539	36.3	197.2	25100	2324	2323	3.763
Iodobenzene	1.86059	183.45	448.0	(33910)	5846	5814	3.777
Chlorobenzene	1.12786	132.0	360.0	33910	3670	3654	3.777
Fluorobenzene	1.04653	85.2	286.55	33910	3542	3541	3.790
Bromobenzene	1.52182	156.0	397.0	(33910)	4879	4853	3.799
Di-isobutyl	71021	109.2	276.8	18660	2369	2366	3.808
Ether	73620	34.6	194.4	27060	2624	2622	3.811
Normal Hexane	67696	68.95	234.8	22510	2345	2344	3.829
Normal Heptane	70048	98.4	266.9	20415	2344	2341	3.855
Methyl Isobutyrate	91131	92.3	267.55	25750	3017	3012	3.862
Normal Octane	71848	125.8	296.2	18730	2351	2357	3.863
Propyl Formate	92868	80.9	264.85	30440	3065	3063	3.868
Ethyl Formate	94802	54.3	235.3	35590	3232	3232	3.885
Methyl Propionate	93871	79.7	257.4	30030	3123	3124	3.904
Ethyl Butyrate	92006	102.75	281.25	25600	3003	3002	3.905
Methyl Propionate	91240	99.0	272.9	25210	2969	2965	3.912
Methyl Formate	1.00319	31.9	214.0	45030	3494	3489	3.926
Propyl Acetate	91016	101.55	276.2	25210	2964	2957	3.934
Ethyl Acetate	95932	57.1	233.7	35180	3255	3252	3.942
Propyl Alcohol	92436	77.15	250.1	28880	3081	3077	3.944
Ethyl Alcohol	81930	97.4	263.7	38120	2752*	2734	3.995
Methyl Alcohol	80625	78.3	243.1	47850	2705*	2725	4.024
Acetic Acid	81020	64.9	240.0	59760	3511	3506	4.549
	1.06970	118.5	321.6	43400			4.986

difference, 0.26 per cent. ; in fourteen cases it is less than 0.1 per cent.

The alterations in the order of the substances in the tables (depending on $\frac{D_c}{D'_c}$) are few in number ; di-isopropyl is brought next to isopentane ; the four halogen derivatives of benzene are brought together, whereas in the old table bromobenzene was separated from the others ; lastly, the new order of the alcohols is propyl, ethyl, methyl in place of ethyl, propyl, methyl.

In both tables the iso- and di-isocompounds have lower values of $\frac{D_c}{D'_c}$ than the corresponding normal compounds.

It is perhaps worth remarking that if, in the formula $\alpha = \frac{\alpha T_c}{D_c}$, we take the value of α in the formula with three constants instead of in that with two, and if we exclude the alcohols and acetic acid, the variation in α is much smaller than before, the extreme values being .916 and 1.039 as against .882 and 1.090, and the change is especially marked in the case of the hydrocarbons, for which the new constants range from .916 to .968 as against .882 to 1.075. Now α in the formula $D_t = D_0 + \alpha t + \beta t^2$ differs but little from what it would be in the formula $D_t = D_0 + \alpha t$ if we were to take only the densities below the boiling-point, and as the variation of α is smaller in this case, it is the more remarkable that this constant should be so very low (.7675) for chlorine.

In this respect chlorine resembles the alcohols ($\alpha = .717$, .746, and .844), but the critical densities of the alcohols are abnormally high whilst that of chlorine appears to be very low. It would be of considerable interest if the densities of the saturated vapour of chlorine could be determined at high temperatures so that the values of α , α , and D_0 could be ascertained with certainty, but the experimental difficulties would be very great.

GENERAL CONCLUSIONS.

1. The law of Cailletet and Mathias is very nearly, though in most cases not absolutely, true ; it appears to be only

strictly true when the ratio of the actual to the theoretical density at the critical point $\left(\frac{D_c}{D'_c}\right)$ has the normal value 3.77.

2. The curvature of the "diameter" is generally smaller the nearer $\frac{D_c}{D'_c}$ approaches the normal value, and the nearer $\alpha \left(= \alpha \frac{T_c}{D_c}\right)$ approaches the value 0.93.

3. The curvature is in nearly every case in opposite directions according as $\frac{D_c}{D'_c}$ is greater or less than 3.77, and as α is greater or less than 0.93, and is such that in the formula $D_t = D_0 + \alpha t + \beta t^2$ β is positive when $\frac{D_c}{D'_c}$ is lower than 3.77 and negative when it is higher, α being negative in every case.

4. The curvature is generally so slight that the critical density may be calculated from the mean densities of liquid and saturated vapour at temperatures from about the boiling-point to within a few degrees of the critical point by means of the simpler formula $D_t = D_0 + \alpha t$ with an error rarely exceeding 0.25 per cent. and generally not exceeding 0.1 per cent.

5. If, however, the critical density be calculated from the mean densities at low temperatures (say below the boiling-point) only, the error may be considerable; in the case of normal decane it is probably between 5 and 6 per cent.

6. As has been pointed out by M. Guye (*Archives des Sciences Phys. et Nat.* 1894, series 3, vol. xxxi.) the law does not, as a rule, hold good at all for substances the molecules of which differ in complexity in the gaseous and liquid states.

APPENDIX.

Since this paper was written Mr. K. Tsuruta has kindly sent me a copy of his 'Thermodynamic Notes,' No. 10 (Phys. Rev. 1900, x, p. 116) in which he discusses the "law of straight diameter" as applied to benzene. The conclusion he arrives at is that whilst the mean densities obey the law "in quite a satisfactory manner" not only from 80° to the critical-point, but also from 80° down to the triple point, yet a more minute examination showed the so-called diameter "to consist of two nearly straight parts meeting somewhere near the temperature

180° C., or, more strictly, to be a curve whose curvature is so slight that it can be so described."

This conclusion is practically in agreement with that stated in this paper.

DISCUSSION.

Mr. ROSE-INNES said that in his paper the author had used the generalizations of van der Waals, although the author himself had shown that they were not strictly true.

Dr. YOUNG said that the generalizations held accurately in some cases, although they did not in others. In all cases in which molecular association or dissociation did not occur they were approximately true, and it was advisable to study them in order, if possible, to ascertain the cause of the small deviations.

XXXI. *On the Concentration at the Electrodes in a Solution, with special reference to the Liberation of Hydrogen by Electrolysis of a Mixture of Copper Sulphate and Sulphuric Acid.* By HENRY J. S. SAND, Ph.D., Bowen Research Scholar at Mason University College, Birmingham*.

CONTENTS :—Historical introduction.—Theoretical consideration of the Liberation of Two Constituents at an Electrode.—Calculation of the Concentration in a Solution contained in a cylindrical vessel, across one end of which a constant flow of salt is taking place.—Application of results to obtain Values for the Concentration at the Electrode of the Solution of a single Salt and of a Mixture.—Experimental determination of the Time required till Hydrogen appears during Electrolysis of an Acid solution of Copper Sulphate.—A new method for determining the Diffusion-Coefficient of Copper Sulphate.—Experiments to show the great influence of Convection-Currents on the quantity of Hydrogen given off in the Electrolysis of an Acid Solution of Copper Sulphate.—Summary of results.

SINCE the electrolysis of mixtures first attracted the attention of scientists, three distinct views have been held about the processes which take place at the electrodes.

In 1857 Magnus† put forward the theory that in the

* Read October 26, 1900.

† Pogg. Ann. cii. p. 17.