MOLECULAR ATTRACTION, IV. ON BIOT'S FORMULA FOR VAPOR PRESSURE AND SOME RELATIONS AT THE CRITICAL TEMPERATURE

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The $\frac{\partial P}{\partial T}$ of a liquid

In a preceding paper¹ we examined the following equation, which had been proposed on theoretical grounds by Mr. H. Crompton:

$$(1) \quad L = 2 \int_v^V p \partial v = 2RT \log_e \frac{d}{D} = \frac{9.154}{m} T \log \frac{d}{D} \text{ cal.}$$

(L is heat of vaporization, v and V denote volume of liquid and vapor, d and D the density of liquid and vapor, p is pressure, T is temperature, m is molecular weight, R is the constant of the gas equation, $PV = RT$.)

It was there shown that this equation gives at low temperatures where the vapor pressure is small, results for the heat of vaporization that are invariably and usually very considerably too large. But at the higher temperatures examined, that is as the critical temperature is approached, the results given by the equation appeared to be correct. The evidence there given as to the correctness of this equation at high temperatures was very considerable and justified further use of the equation. Therefore in that paper we combined the usual thermodynamical equation for calculation of the heat of vaporization,

$$(2) \quad L = \frac{T}{J} (V - v) \frac{\partial P}{\partial T} = 0.0431833 T(V - v) \frac{\partial P}{\partial T} \text{ cal.}$$

with the equation of Crompton given above, and obtained equation 15 of that paper, *viz.*:

$$(3) \quad \frac{\partial P}{\partial T} = \frac{287500}{m} \frac{\log \frac{V}{v}}{V - v}$$

We there showed that the limit approached by this equation as

¹ Jour. Phys. Chem., 8, 593 (1904).

the critical temperature was approached and V approached v in value, was,

$$(4) \quad \frac{\partial P}{\partial T} = \frac{124860}{m V}.$$

We at that time overlooked the fact that this equation 4 could be expressed in the very simple form,

$$(5) \quad \frac{\partial P}{\partial T} = \frac{2 R}{V}.$$

Here V is the critical volume and R is the usual gas constant, and we have the striking conclusion that *at the critical temperature the $\frac{\partial P}{\partial T}$ of the liquid (vapor) is exactly twice what it would be for that substance as a perfect gas occupying the same volume.* Expressed in this form the bearing of equation 3, or its limiting forms, on the kinetic relations of a liquid and its vapor, assumes more importance and justifies closer study.

Accordingly by means of equation 4, we calculated, and give in Table I, the values of the $\frac{\partial P}{\partial T}$ at the critical temperature for twenty substances. The critical data used is that given by Dr. Young.¹ This data is more correct than that given in earlier papers. (We would here note that in the third paper on Molecular Attraction² we overlooked this corrected data, but have since repeated the calculations there given using the corrected data and find no material change in the results or conclusions there expressed.)

For comparison with these values the $\frac{\partial P}{\partial T}$ can be calculated from any equation connecting vapor pressure and temperature. Of the numerous equations that have been proposed the one usually known as Biot's has proved by far the most serviceable. It takes the form,

$$(6) \quad \text{Log } P = A + b.\alpha^t + c.\beta^t.$$

By differentiating and changing to Napierian logarithms we get

$$(7) \quad \frac{\partial P}{\partial T} = 5.3019 P(b.\log \alpha.\alpha^t + c.\log \beta.\beta^t).$$

¹ Phil. Mag. [5], 50, 291 (1900).

² Jour. Phys. Chem., 8, 593 (1904).

Since we had previously used Biot's formula for calculating heats of vaporization more directly, we found it easier to throw equation 7 into the form,

$$(8) \quad \frac{\partial P}{\partial T} = 0.031414 \text{ PA,}$$

where $A = 168.775 (b \log \alpha \cdot \alpha^t + c \log \beta \cdot \beta^t)$.

The constants for this equation have already been given¹ for all of the substances examined, except those noted below.

Ethyl oxide. $A = \text{antilog } (\bar{1}.9882227 - 0.00172541 t) + \text{antilog } (\bar{1}.7399799 - 0.00869664 t), t = t^\circ \text{C.}$

Benzene. $A = \text{antilog } (\bar{1}.4256719 + 0.0001302029 t) + \text{antilog } (0.1799122 - 0.00410411 t), t = t^\circ \text{C.}$

Methyl alcohol. $A = \text{antilog } (\bar{1}.5561254 - 0.00011584 t) + \text{antilog } (0.2151667 - 0.00400204 t), t = t^\circ \text{C.}$

Ethyl alcohol. $A = \text{antilog } (\bar{2}.3965216 + 0.003377538 t) + \text{antilog } (0.3342413 - 0.00317576 t), t = t^\circ \text{C.}$

Propyl alcohol. $A = \text{antilog } (\bar{2}.8340346 + 0.001641423 t) + \text{antilog } (0.3135244 - 0.00342975 t), t = t^\circ \text{C} - 20.$

The constants for ethyl formate and methyl acetate were kindly sent me by Dr. Young (work yet unpublished) and the constants for methyl formate I have calculated and will publish later.

The values of the $\frac{\partial P}{\partial T}$ at the critical temperature as obtained from these Biot equations are shown in Table I.

Of the twenty substances compared in Table I it will be seen that the $\frac{\partial P}{\partial T}$ from equation 4 has a higher value than the $\frac{\partial P}{\partial T}$ calculated from Biot's formula in all cases except di-isobutyl, normal octane, and ethyl alcohol. The difference is usually very marked.

In work done upon an equation of the form, $P = bT - a$, Ramsay and Young² made a study of the $\frac{\partial P}{\partial T}$ of ether at constant

¹ Jour. Phys. Chem., 8, 383 (1904).

² Phil. Mag. [5], 23, 435 (1887).

TABLE I

Substance	Critical temperature	$\frac{\partial P}{\partial T}$ from Equation 4	$\frac{\partial P}{\partial T}$ from Biot	Δ	A
Ethyl oxide	194.45°C	441.9	391.6	50.3	0.46068
Di-isopropyl	227.35	349.6	321.0	28.6	0.43795
Di-isobutyl	276.8	258.8	261.6	-2.8	0.44672
Isopentane	187.8	405.7	367.8	37.9	0.46822
Normal pentane	197.2	402.3	364.8	37.5	0.46331
Normal hexane	234.8	339.9	315.9	24.0	0.44826
Normal heptane	266.85	291.9	286.9	5.0	0.44782
Normal octane	296.2	254.5	256.8	-2.3	0.43647
Benzene	288.5	487.0	445.4	41.6	0.38961
Hexamethylene	279.95	406.0	376.0	30.0	0.39583
Fluo-benzene	286.55	460.1	430.7	29.4	0.40428
Carbon tetrachloride	283.15	452.7	416.7	36.0	0.38808
Stannic chloride	318.7	355.2	332.5	22.7	0.37689
Methyl formate	214.0	725.6	619.2	106.4	0.43872
Ethyl formate	235.3	545.0	479.7	65.3	0.43091
Methyl acetate	233.7	548.3	502.3	46.0	0.45454
Methyl alcohol	240.0	1061.1	971.1	90.0	0.51729
Ethyl alcohol	243.1	747.0	796.7	-49.7	0.52998
Propyl alcohol	263.7	568.3	562.4	5.9	0.47181
Acetic acid	321.65	729.2	574.6	154.6	0.42066

volume, Young,¹ later a similar study for iso-pentane, and Rose-Innes and Young² correspondingly for normal pentane. At the critical volume the value of the $\frac{\partial P}{\partial T}$ obtained at constant volume becomes identical with the value of the $\frac{\partial P}{\partial T}$ denoting the increase in vapor pressure of the liquid. Therefore it is possible in these three cases by comparison with the values of the $\frac{\partial P}{\partial T}$ obtained in the above papers to determine whether the values of the $\frac{\partial P}{\partial T}$ calculated from Biot's formula or those obtained from Equation 4 are correct. The result is shown below, the values of the $\frac{\partial P}{\partial T}$ at the exact critical volume having been obtained from the

¹ Phil. Mag. [5], 38, 569 (1894).

² Ibid. [5], 47, 353 (1899).

above-mentioned papers by interpolation and entered in the column marked "Observed."

Substance	Volume	From Biot	Equation 4	Observed
Ether	3.814	391.6	441.9	436
Isopentane	4.268	367.8	405.7	401 to 411
Normal pentane	4.305	364.8	402.3	406.7

In every case the values accord to within the limit of experimental error with the values derived from Equation 4, and are uniformly higher than the values derived from Biot's equation. (It is not possible to extend the comparison to the alcohols and acetic acid studied by the observers above mentioned, for these liquids are associated and Equation 4 depending on the molecular weight, could not give correct results.)

On Biot's formula for vapor pressure

It seemed to us reasonable to conclude from the above comparison that the ratios of the $\frac{\partial P}{\partial T}$ calculated from Equation 4 at the critical temperature and shown in Table I were the correct values and that the values obtained from Biot's formula were in error. Fortunately we had a means of verifying this conclusion directly.

If the vapor pressure curve be plotted against the temperature, the $\frac{\partial P}{\partial T}$ is the tangent to the curve. Assuming that Biot's formula does correctly represent the vapor pressures until the critical temperature is approached (an assumption justified by a very careful examination of the curves over the entire range of temperature) it is evident that if the $\frac{\partial P}{\partial T}$ calculated from Biot's formula then becomes too low it must be because the vapor pressure curve as calculated from Biot's formula is below the true vapor pressure curve. We accordingly subtracted the observed vapor pressures from the calculated in the immediate neighborhood of the critical temperature and obtained the results shown in Table II. In

every case except normal octane, stannic chloride, and the associated substances (methyl alcohol, ethyl alcohol, and acetic acid), the calculated minus the observed vapor pressures does give negative differences at the highest temperature compared (usually the critical temperature itself). With regard to these five exceptions, the associated substances cannot give exactly correct results by the use of Equation 4 and their evidence does not, therefore, bear upon that equation. Normal octane and stannic chloride are the only substances whose divergence can be considered as evidence against the conclusion above derived and it is sufficient to point out in explanation a remark made by Dr. Young¹ when the vapor pressures of normal octane were published. He there states that the observed values of the vapor pressure above 280° C for *normal octane, stannic chloride, and acetic acid*, are probably *too low* owing to an error in the temperature scale, *i. e.*, in the boiling-points of the liquids used as a heating jacket.

A close examination of the observed and calculated vapor pressure curves reveals the fact that no matter how the constants for Biot's formula be altered, they cannot exactly represent the true vapor pressures in the neighborhood of the critical temperature. The deviation is very slight, usually negligible when the vapor pressure is considered, because the proportional error is very small. But when the $\frac{\partial P}{\partial T}$ is considered the proportional error is very large.

Since Biot's formula was empirical and in the immediate neighborhood of the critical temperature was forced to fit a curve it could not exactly follow, it usually happens that the curve of observed vapor pressures cuts the curve of calculated vapor pressures in the neighborhood of the critical temperature, the observed vapor pressure curve having, of course, the steeper trend. This is at once evident on reference to Table II by the change from positive to negative values of the differences between the calculated and observed vapor pressures.

¹ Jour. Chem. Soc., 77, 1147 (1900).

We would here point out the great accuracy of these measurements made by Drs. Ramsay and Young and by Dr. Young and his co-workers. The conclusion that the calculated minus the observed vapor pressure should be negative near the critical temperature was wholly theoretical on our part. That we should be able at once to verify this conclusion from the measurements when the differences were so small as to have been laid by the observers themselves on the errors of measurement (the regularity of the differences having escaped observation) speaks for itself as to their accuracy and skill. The observed and calculated vapor pressure lines are almost indistinguishable even at the critical temperature and when drawn to a large scale.

TABLE II

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Ethyl oxide	170°C	300.5	303.5	18622	18671	— 49
	180	336.3	345.2	21804	21775	29
	185	354.9	368.8	23532	23623	— 91
	190	374.1	399.5	25355	25513	—158
	192	382.2	415.8	26111	26331	—220
	193	385.8	429.7	26495	26800	—305
	194.45	391.6	441.9	27060		
Di-isopropyl	180	186.6	187.2	11536	11535	1
	200	236.5	236.0	15752	15693	59
	220	296.2	302.6	21062	21009	53
	225	312.9	327.1	22585	22588	— 3
	227.35	321.0	349.6	23330	23360	— 30
Di-isobutyl	220	128.6	123.0	7941	7937	4
	240	165.7	155.6	10883	10905	— 22
	260	212.5	196.9	14660	14651	9
	270	240.4	225.7	16929	16905	24
	274	253.9	240.1	18006		
	276.8	261.6	258.8	18640	18660	— 20

TABLE II—(Continued)

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Isopentane	140	204.4	208.3	11620	11634	— 14
	160	264.0	267.7	16285	16320	— 35
	180	335.9	348.1	22262	22270	— 8
	185	356.1	377.6	23992	24000	— 8
	187	364.4	393.2	24713	24730	— 17
	187.4	366.4	400.1	24854	24880	— 26
	187.8	367.8	405.7	25005	25018	— 13
Normal pentane	160	235.0	237.4	14032	14060	— 28
	180	299.7	303.5	19362	19345	17
	190	336.5	347.4	22540	22500	40
	195	355.9	378.1	24271	24255	16
	197	363.8	397.2	24991	25020	— 29
	197.2	364.8	402.3	25063	25100	— 47
Normal hexane	180	163.8	162.9	9659	9650	9
	200	210.2	207.3	13385	13348	37
	220	266.4	264.8	18133	18100	33
	230	299.0	303.8	20957	20955	2
	234	313.0	328.2	22181	22220	— 39
	234.8	315.9	339.9	22433	22510	— 37
Normal heptane	220	162.0	153.2	10130	10105	25
	240	207.6	194.8	13811	13790	21
	260	264.4	252.5	18511	18470	41
	264	277.4	269.5	19595	19610	— 15
	266.5	285.8	286.4	20300		
	266.85	286.9	291.9	20399	20430	— 31
Normal octane	240	130.9	122.8	8184.5	8219	—34.5
	260	167.5	154.8	11156	11185	— 29
	280	212.6	196.7	14942	15015	— 73
	290	239.0	224.8	17198	17126	72
	296.2	256.8	254.5	18734	18730	4
Benzene	240	269.5	273.7	19369	19352	17
	260	333.0	337.4	25376	25329	47
	280	408.9	420.0	32772	32782	10
	288.5	445.4	487.0	36409	36395	— 14

TABLE II—(Continued)

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Hexamethylene	240	246.7	249.8	17961	17973	— 12
	260	305.2	307.6	23461	23439	22
	270	338.9	344.4	26680	26667	13
	277	364.6	379.3	29140	29206	— 66
	279	372.3	394.0	29878		
	279.95	376.0	406.0	30234	30260	— 26
Fluo-benzene	240	258.5	260.4	18190	18161	29
	260	322.3	321.4	23977	23960	17
	280	400.9	405.3	31182	31217	— 35
	286.55	430.7	460.1	33905	33912	— 7
Carbon tetrachloride	240	266.8	271.7	19596	19633	— 37
	260	328.6	333.4	25532	25528	4
	280	402.9	415.6	32825	32825	0
	283.15	416.7	452.7	34114	34181	— 67
Stannic chloride	240	148.7	166.9	9915	9915	0
	260	184.9	212.9	13242	13290	— 48
	280	227.3	269.9	17351	17454	— 103
	310			25294	25079	215
	318.7	332.5	355.2			
	319.35			28283	28079	204
Methyl formate	180	431.8	443.5	27163	27040	123
	200	537.8	569.6	36839	36685	154
	210	595.4	661.1	42502	42510	— 8
	213.5	616.2	714.8	44622	44670	— 48
	214.0	619.2	725.6	44932	45030	— 98
Ethyl formate	160	199.8	200.6	10830	10847	— 17
	180	259.3	259.1	15405	15385	47
	200	329.0	330.8	21271	21148	123
	220	409.8	422.9	28640	28527	113
	230	454.7	483.1	32961	32968	— 7
	235.3	479.7	545.0	35436	35535	— 99

TABLE II—(Continued)

Substance	Temperature	$\frac{\partial P}{\partial T}$ from Biot	$\frac{\partial P}{\partial T}$ from Equation 3	Pressure		Δ
				Calc.	Obs.	
Methyl acetate	180	262.8	258.0	15152	15118	34
	200	338.8	332.3	21146	21085	61
	220	429.8	429.3	28804	28705	99
	230	481.8	497.9	33360	33358	2
	233.7	502.3	548.3	35180	35212	— 32
Methyl alcohol	180	411.1	385.0	20016	20089	— 73
	200	560.8	520.4	29688	29787	— 99
	220	747.9	709.5	42676	42573	103
	230	851.9	830.4	50651	50414	237
	238.5	951.7	973.3	58310	58329	— 19
	240.0	971.1	1061.1	59759	59660	99
Ethyl alcohol	200	430.8	353.0	22182	22164	18
	220	576.6	491.5	32196	32097	99
	240	763.7	675.0	45519	45504	15
	242.5	790.0	731.2	47463		
	243.1	796.7	747.0	47939	47850	89
Propyl alcohol	220	334.0	293.9	18667	18679	— 12
	240	428.0	390.1	26263	26194	69
	260	540.0	505.1	35908	36103	— 195
	263.7	562.4	568.3	37947	38120	— 173
Acetic acid	280	367.5	426.8	24055	24123	— 68
	300	460.3	534.9	32312	32043	269
	310	511.4	600.7	37168	36943	225
	320	565.4	710.9	42550	42553	— 3
	321.65	574.6	729.2	43480	43404	76

In order to show that Equation 4 does give results in accord with Biot's formula at points considerably below the critical temperature we give in Table II the values of the $\frac{\partial P}{\partial T}$ calculated from both formulas at intervals for some 50° C below the critical temperature. We have already pointed out that Equation 4 itself becomes inaccurate at yet lower temperatures.

Correct values for μ' near the critical temperature

Since Equation 4 enables us to obtain in the neighborhood of the critical temperature more nearly correct values for the $\frac{\partial P}{\partial T}$ than we had been able to obtain in previous papers when working with Biot's formula we concluded to use these values and test more thoroughly the equation,

$$(9) \quad \frac{L - E_2}{V^2 \bar{a} - V^2 \bar{D}} = \text{constant} = \mu'$$

discussed in previous papers¹. If the value of the $\frac{\partial P}{\partial T}$ from Equation 3 be substituted in the thermodynamical equation, 2, the values of the heat of vaporization so calculated are the same as those obtained from Equation 1. Therefore using these values and substituting them in Equation 9 we obtain the corrected values for the constant. The results so obtained at those points nearest the critical temperature are given in Table III under the heading "New." For comparison we give under heading "Old" the values that we had previously obtained for μ' at this same temperature when using the $\frac{\partial P}{\partial T}$ obtained from Biot's formula in calculating the heats of vaporization thermodynamically. Also we give under the heading "Mean," the average value of the constant previously adopted. Agreement is not of course to be expected for the four associated substances last shown in the table. For the other substances there is little question but that the constants so obtained agree with the mean values to within the limit of experimental error except in the cases of di-isobutyl, normal heptane, normal octane, and methyl acetate. We are unable to explain the smaller values obtained from these four substances but the proof that Equation 9 does hold as near the critical temperature as it is possible for measurements to be made is now complete for ethyl oxide, di-isopropyl, isopentane, normal pentane, normal hexane, benzene, hexa-methylene, fluo-benzene, carbon tetrachloride, stannic chloride, methyl formate, and ethyl formate.

¹ Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904).

TABLE III

Substance	Temperature	Old μ'	New μ'	Mean μ'	Critical temperature	From Equation 12 μ'	$\frac{PVm}{T}$
Ethyl oxide	193	90.7	102.0	104.4	194.4	102.1	16360
Di-isopropyl	225	92.0	96.8	98.1	227.4	96.5	16660
Di-isobutyl	274	86.4	82.3	86.3	276.8	80.7	16370
Isopentane	187.4	99.3	107.0	105.4	187.8	107.0	16710
Normal pentane	197	98.8	109.9	109.9	197.2	109.4	16570
Normal hexane	234	94.2	99.5	102.85	234.8	99.2	16290
Normal heptane	266.5	90.8	91.0	98.75	266.9	90.8	16170
Normal octane	290	91.0	84.8	93.0	296.2	84.2	16140
Benzene	280	107.8	111.2	109.5	288.5	110.5	16610
Hexamethylene	279	98.1	104.7	103.6	280.0	104.5	16820
Fluobenzene	280	84.7	85.75	85.6	286.55	85.2	16440
Chlorobenzene	—	—	—	81.2	360.0	81.5	16490
Brombenzene	—	—	—	56.1	397.0	56.3	16380
Iodobenzene	—	—	—	44.4	448.0	43.8	16500
Carbon tetrachloride	280	43.9	45.5	44.1	283.15	45.3	16940
Stannic chloride	280	22.15	26.96	26.04	318.7	25.87	16680
Methyl formate	213.5	101.2	120.1	121.5	214.0	119.8	15910
Ethyl formate	234	94.0	104.4	107.2	235.3	103.9	16040
Methyl acetate	233	96.6	103.8	109.5	233.7	103.6	15800
Methyl alcohol	238.5	259.4	264.3	305.0	240.0	262.4	13705
Ethyl alcohol	242.5	197.2	178.9	241.2	243.1	179.9	15495
Propyl alcohol	260	157.0	144.6	199.2	263.7	143.7	15590
Acetic acid	320	116.4	150.6	—	321.6	150.7	12502

The value of μ' at the critical temperature

It is possible to extend this proof quite to the critical temperature itself. Substituting in Equation 9 the value of L given by the thermodynamical equation, 2, and the value of $E_1 = .0431833P(V - v)$, we have

$$(10) \quad \frac{.0431833 \left(T \frac{\partial P}{\partial T} - P \right) (V - v)}{V^2 \bar{d} - V^2 \bar{D}} = \mu',$$

and obtaining the limit of this equation as V approaches v in value we have for the equation at the critical temperature, where $V = v$, the form

$$(11) \quad .04955 V^{\frac{4}{3}} \left(T \frac{\partial P}{\partial T} - P \right) = \mu'.$$

As we have shown, the most correct value for the $\frac{\partial P}{\partial T}$ available at this temperature is that given by Equation 4 and substituting this value in the equation we get,

$$(12) \quad \mu' = V^{\frac{1}{3}} \left(\frac{11.924T}{m} - .04955PV \right).$$

This equation is the same as Equation 17 of the third paper¹. Here V , T , and P , are the critical volume, temperature, and pressure, respectively, and m is the molecular weight of the substance under consideration. The equation is interesting because it gives a method for calculating the constant of molecular attraction μ' in terms of the critical constants and the molecular weight of the substance. Since the molecular weight enters into the equation it evidently cannot be applied to associated substances. Again using the critical data already referred to, given by Young, the values obtained from this equation are shown in Table III, above. Except for di-isobutyl, normal heptane, normal octane, methyl acetate, and to a less degree for ethyl formate, the agreement with the mean values of μ' is excellent and we may therefore regard the truth of Equation 9 as having been established at the critical temperature itself for fifteen of the nineteen substances under consideration. (Ethyl formate decomposes slightly at the higher temperatures which is sufficient to account for the divergence, three percent, there observed.) We have already shown that normal heptane and normal octane give constant values for μ' in Equation 9 over a range of more than 200° C in temperature. We have unpublished results showing the same to be true for methyl acetate. Di-isobutyl did give a variation of several percent at low temperatures, a divergence that we think was sufficiently explained.² It would seem probable therefore that the divergences shown by these four substances at the critical temperature must be due to some change or decomposition taking place in the substance at that temperature and that Equation 9 is applicable for all normal substances quite up to the critical temperature.

¹ Jour. Phys. Chem., 8, 593 (1904).

² Ibid., 8, 595 (1904).

Ratio of the theoretical to the actual critical density

In a preceding paper¹ we showed that the molecular attraction at unit distance, μ , was equal to $c\mu'\sqrt[3]{m}$. Therefore we have from Equation 12,

$$(13) \quad \mu = c\sqrt[3]{mV} \left(\frac{11.924T}{m} - .04955PV \right).$$

In the same paper on the assumption that the critical temperature was the point where the kinetic energy of the molecules was just balanced by the molecular attraction we derived Equation 24 of that paper, viz.:

$$(14) \quad \mu = c' \frac{T}{m} \frac{\sqrt[3]{m}}{d},$$

where T is the critical temperature and d is the critical density. We can now combine this value of μ with the value of μ given in Equation 13 and obtain,

$$(15) \quad c' \frac{T}{m} \frac{\sqrt[3]{m}}{d} = c \sqrt[3]{mV} \left(\frac{11.924T}{m} - .04955PV \right),$$

whence,

$$(16) \quad \frac{PVm}{T} = \text{constant}.$$

We show the values of $\frac{PVm}{T}$ in Table III and it will be seen that hexamethylene and carbon tetrachloride alone (the associated substances being excepted) give a value more than three percent from the average value 16293.

$\frac{.0416014Pm}{T}$ is the theoretical critical density and Equation 16 is really the ratio of the theoretical, D_c , to the actual critical density, d_c , and can take the form,

$$(17) \quad \frac{D_c}{d_c} = \text{constant}.$$

The relation in this form has been fully discussed by Dr. Young.² It here appears as a necessary consequence of the ideas that we

¹ Jour. Phys. Chem, 8, 630 (1904).

² Phil. Mag., [5] 50, 291 (1900).

have advanced though we did not foresee that such would be the case, and hence are justified in considering the deduction of this relation as further evidence that those fundamental ideas upon which this series of papers is based are correct.

It may seem unusual that we should have been able to derive two different equations for μ (Equations 13 and 14) in terms of the critical constants. This is due to the fact that the critical temperature besides possessing the property that the molecular attraction just balances the kinetic energy of the molecules—the relation upon which Equation 14 is based—can also be viewed as a boiling-point and from this point of view permits the deduction of Equation 13. We hope shortly to complete a paper applying these ideas of molecular attraction more fully to the boiling-point.

We should also point out that by combining Equation 11 with Equation 14, we get

$$(18) \quad \frac{T}{m} = cV \left(\frac{T \partial P}{\partial T} - P \right),$$

where c is a constant. This equation can be solved so as to give any one of the variables at the critical temperature in terms of the others and the molecular weight. It is not feasible now to further examine this equation, since the only correct values for the $\frac{\partial P}{\partial T}$ are obtained from Equation 4 and this at once reduces the equation to the form of Equation 16.

Dr. Young¹ has shown that the average constant of Equation 17 is $\frac{1}{3.827}$. Since the theoretical critical pressure is therefore 3.827 times the actual critical pressure it follows from the gas law and Equation 5 that at the critical temperature,

$$(19) \quad \frac{\partial P}{\partial T} = \frac{7.654P}{T}.$$

This equation can be obtained directly from Equation 18 but the constant is then unknown.

SUMMARY.

1. It is shown that the $\frac{\partial P}{\partial T}$ for a liquid (vapor) at the critical temperature is exactly twice what it would be for the same substance as a perfect gas occupying the critical volume.

2. It is shown that Biot's formula for vapor pressure cannot be made exactly to fit the true vapor pressure curve in the immediate neighborhood of the critical temperature. When the pressure is considered, the proportional error is very small. When the $\frac{\partial P}{\partial T}$ is considered, the proportional error is large and the values obtained from Biot's formula are too small.

3. The equation, $\frac{L - E_1}{\frac{1}{V}d - \frac{1}{V}D} = \mu'$, where μ' is the constant of molecular attraction, is shown to be applicable with exactness in the immediate neighborhood of, and at, the critical temperature for fifteen out of nineteen substances considered. The equation has already been proved accurate at lower temperatures.

4. It is shown that the constant of molecular attraction, μ' , can be calculated from the critical constants and the molecular weight.

5. The known fact that the ratio of the theoretical critical density to the actual critical density is a constant for all substances is shown to follow necessarily from the fundamental ideas and equations upon which this series of papers is based.

*University of North Carolina,
April 3rd, 1905.*