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Capillary Attraction in Relation to Chemical
Composition, on the Basis of
R. Schiff's Data.

By K. Ikeda.

Post Graduate Student in the Chemical
Institute, College of Science.

Many physical properties of solid and liquid substances can be so measured and expressed that the quantity for a molecule is the sum of the quantities for its constituent atoms. The heat capacity of inorganic solids, the space occupied by liquids at their boiling points, refraction of light, and rotation of the plane of polarization under magnetic influence, are well known examples. The heat capacity of organic liquids under certain conditions and the magnetic behavior of the same probably belong to the list, and there is reason to believe that the heat of formation from dissociated atoms is also of the same description.

All these properties can be represented by the following simple formula,

$$F(\alpha, \beta, \gamma, \dots, K) = ma + nb + pc + \dots$$

where K is the duly measured property, under consideration, of a compound whose chemical formula may be written $A_m B_n C_p \dots$; while $\alpha, \beta, \gamma, \dots$ are functions of other properties belonging to the substance, and a, b, c, \dots are special values for the atoms of the constituents A, B, C, \dots .

In all known instances α, β, γ , &c, as well as F , are very simple functions.

It is the endeavor of the present paper to show that capillary attraction of organic liquids belongs to the above mentioned category of physical properties, and can be represented by the same general formula.

That there is a well defined relation between capillary constants of liquid substances and their molecular composition has been put beyond all doubt by the extensive and elaborate experimental investigations of R. Schiff. He has chosen boiling points as the temperature of physical comparability, and expressed the relation between capillary constants at these points and the chemical composition by the formula

$$N = \frac{\epsilon^{a-bH}}{H},$$

in which N stands for the relative number of molecules raised in a capillary tube, H is the sum of the special values for the constituent atoms referred to hydrogen as unity, ϵ is the base of the Napierian logarithms, while a and b are constants. This equation accords fairly well with the experimental results; but it is hard to see why such a relation should exist between N and H , or rather the meaning of the latter term is very difficult to make out. The expression, indeed, claims no higher title than that of being strictly empirical; still it is better to use those terms only, to which some probable meaning, at least, can be assigned. The two formulæ about to be proposed are in no way superior to Schiff's as far as purely theoretical consideration goes, for they pretend to no theoretical ground whatsoever. Still they seem to be more rational inasmuch as the terms involved have some meaning, and besides agree better with the observed results, as will be shown later on. The new equations are of the same form as the general expression already given, and show the relation between capillary constants and molecular volumes in a very clear manner, although it is rather difficult to understand why they

should be of these particular forms. The formulæ may be written thus :

$$K = \frac{ma + nb + pc + \dots}{V^{\frac{2}{3}}} \dots (I_a)$$

or $KV^{\frac{2}{3}} = ma + nb + pc + \dots (I_b)$

and $K^{\frac{1}{2}}V^{1.18} = ma' + nb' + pc' + \dots (II).$

Here K stands for the capillary rise of a liquid multiplied by its specific gravity, both being taken at the boiling point. V is the molecular volume, or the molecular weight divided by the specific gravity ; a , b , c , &c and a' , b' , c' , &c are quantities having particular values for A , B , C , etc., and may be called atomic capillary constants.

If we assume the principle of molecular volumes to be rigorously true, then V may be expanded into $ma + nb + pc + \dots$, and K can be found out by mere calculation, provided the molecular constitution of the substance as well as a , b , c , &c or a' , b' , c' , &c and a , b , c , &c are known.

The data for the establishment of the above formulæ have, with only one exception been drawn from Schiff's publications. That exception is heptane for which the calculations have been made from Thorpe's determination. Schiff's investigations cover about one hundred and fifty compounds belonging to various types, and have been communicated to the scientific world in two papers, the first in Liebig's *Annalen* (**223**, 47-106), and the second in the *Gazetta* (**14**, 368-447). As the second periodical is not accessible to me, the information about his second communication is chiefly derived from the abstract published in the *Journal of the Chemical Society, London* (XLVIII, 717-721).* On this account, the data

*There seems to be several misprints in this abstract, for instance nitriles are all spelt nitrites, the critical temperature T for the last seven compounds are all transplanted into the column for molecular volume, while the molecular volume of allylthiocarbimide is made equal to that of the phenyl compound. These considerations make me very unwilling to draw the data from this abstract for a misprint of a figure may vitiate the results of several calculations.

for the recalculation are very imperfect; and as hunting for these in the various periodicals consumes more time than can well be spared, and moreover as the determination of the atomic capillary constant of an element requires the value of K to be known for many compounds of the same type containing the element under consideration, only about one hundred determinations have been submitted to recalculation. Still it is hoped that these will suffice for establishing the approximate validity of the new formulæ.

These one hundred and odd substances consist of compounds of carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine and sulphur. The atomic capillary constants have been calculated from the data, and from these $KV^{\frac{3}{2}}$ & $K^{\frac{1}{2}}V^{1.18}$, as well as K , have been recalculated, with what agreement the following tables will show.

The atomic constants for the various elements (a , b , c , &c. in the formula) used in the calculation of the first table are as follows:

for carbon*	600	in all cases
„ hydrogen	75	„ „ „
„ oxygen	170	in alcohols.
„ „	450	when it is entirely combined with one or more carbon atoms.
„ chlorine	1100	when only one chlorine atom is united with a carbon atom.
„ „	925	when more than two chlorine atoms are united with a carbon atom.
„ bromine	1500	
„ iodine	2150	
„ nitrogen	650	in amines, isocyanates, and nitro bodies.
„ „	450	in nitriles and cyanates,
„ sulphur	1500	

* The value for carbon is most probably higher than this in unsaturated compounds.

sulphur 1150 when two atoms of sulphur are combined with one atom of carbon.

When a polyvalent element is united with the benzene or pyridene ring the value of $KV^{\frac{2}{3}}$ is increased by 300.

TABLE I.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma + nb$ + $pc + \dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma + nb + pc + \dots$	per centage Difference.
Normal Hexane } C_6H_{14}	140.02	4530	4650	2.772	2.845	+120	+2.6
Normal Heptane } C_7H_{16}	162.56	5336	5400	2.575	2.606	+64	+1.2
Diisobutyl C_8H_{18}	184.89	6059	6150	2.410	2.446	+91	+1.5
Diisoamyl $C_{10}H_{22}$	231.80	7718	7650	2.192	2.168	-68	-1.1
Amylene C_8H_{10}	110.18	3564	3750	3.082	3.242	+186	+5.2
Octylene C_8H_{16}	177.61	6074	6000	2.572	2.541	-74	-1.2
Diallyl C_6H_{10}	126.10	4259	4350	3.008	3.072	+91	+2.1
Benzene C_6H_6	96.17	4012	4050	4.254	4.295	+38	+1.0
Toluene C_7H_8	118.25	4748	4800	3.692	3.733	+52	+1.1
Xylene (1:2) C_8H_{10}	139.91	5551	5550	3.354	3.353	-1	0.0
„ (1:3) „	139.69	5544	5550	3.358	3.362	+6	+0.1
„ (1:4) „	140.21	5544	5550	3.340	3.343	+6	+0.1
Ethyl- benzene } „	138.96	5602	5550	3.420	3.388	-52	-1.0
Propyl- benzene } C_9H_{12}	161.82	6427	6300	3.122	3.061	-127	-2.0
Ethyl- toluene } „	161.95	6373	6300	3.092	3.057	-73	-1.1
Mesitylene „	162.41	6234	6300	3.012	3.044	+66	+1.1
Cymene $C_{10}H_{14}$	184.46	6970	7050	2.782	2.814	+80	+1.1

TABLE I.—Continued.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma+nb$ + $pc+\dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma+nb+pc+\dots$	per centage Difference.
Terpene $C_{10}H_{16}$	186.3*	6987	7200	2.748	2.832	+213	+3.0
„ „	196. ?	7166	7200	2.612	2.624	+34	+0.4
Methyl Alcohol } CH_4O	42.72	1066	1070	3.818	3.832	+4	+0.4
Ethyl Alcohol } C_2H_6O	62.19	1731	1820	3.530	3.710	+89	+5.1
Propyl Alcohol } C_3H_8O	81.29	2583	2570	3.524	3.506	-13	-0.5
Isopropyl Alcohol } „	81.69	2513	2570	3.404	3.482	+57	+2.3
Isobutyl Alcohol } $C_4H_{10}O$	101.64	3287	3320	3.208	3.240	+33	+1.0
Isoamyl Alcohol } $C_5H_{12}O$	122.74	4172	4070	3.068	2.994	-102	-2.4
Dimethyl-ethyl-carbinol } „	121.27	4140	4070	3.100	3.047	-70	-1.7
Allyl Alcohol } C_3H_6O	74.11	2495	2420	3.910	3.793	-75	-3.0
Methyl Formate } $C_2H_4O_2$	62.65	2452	2400	4.944	4.839	-52	-2.1
Ethyl Formate } $C_3H_6O_2$	84.57	3074	3150	3.952	4.050	+76	+2.5
Methyl Acetate } „	83.66	3076	3150	4.020	4.117	+74	+2.4
Propyl Formate } $C_4H_8O_2$	106.15	4058	3900	3.710	3.565	+158	+3.9
Ethyl Acetate „	105.78	3854	3900	3.542	3.585	+46	+1.2
Methyl Pro- pionate } „	104.27	3845	3900	3.612	3.664	+55	+1.4
Isobutyl Formate } $C_5H_{10}O_2$	130.74	4829	4650	3.230	3.110	-179	-3.7

* The molecular volume of this compound seems to be abnormally low, being 10 or 9 units less than the calculated, which accounts for the discrepancy as shown in the calculation for Table II. Still it is but fair to confess that several other substances of similar constitution have molecular volumes quite as anomalous. See Lossen's calculation of molecular volumes in Liebig's Annalen(254, 54).

TABLE I.—Continued.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma + nb$ $+ pc + \dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma + nb + pc + \dots$	per centage Difference.	
Propyl Acetate	} $C_5H_{10}O_2$	128.56	4641	4650	3.184	3.190	+9	+0.2
Ethyl Propionate		127.86	4580	4650	3.168	3.217	+70	+1.5
Methyl Butyrate	} "	126.36	4616	4650	3.250	3.274	+34	+0.7
Methyl Isobutyrate		126.44	4535	4650	3.190	3.271	+115	+2.5
Isoamyl Formate	} $C_6H_{12}O_2$	153.22*	5841	5400	3.080	2.847	-441	-7.5
Isobutyl Acetate		152.51†	5610	5400	2.978	2.867	-210	-3.3
Propyl Propionate	} "	150.70	5406	5400	2.922	2.919	-6	-0.1
Ethyl Butyrate		150.25	5356	5400	2.908	2.932	+44	+0.8
Ethyl Isobutyrate	} "	150.68	5246	5400	2.836	2.919	+154	+2.9
Methyl Valerate		148.33	5430	5400	3.006	2.989	-30	-0.6
Isoamyl Acetate	} $C_7H_{14}O_2$	174.60	6372	6150	2.762	2.666	-222	-3.3
Isobutyl Propionate		173.55	6054	6150	2.648	2.690	+96	+1.6
Propyl Butyrate	} "	173.85	6189	6150	2.700	2.683	-39	-0.6
Propyl Isobutyrate		174.20	6056	6150	2.634	2.675	+94	+1.6
Ethyl Valerate	} "	172.99	6139	6150	2.698	2.703	+11	+0.2
Isoamyl Propionate		} $C_8H_{16}O_2$	196.96	6977	6900	2.524	2.496	-77
Isobutyl Butyrate	197.66		6786	6900	2.442	2.483	+114	+1.7
Isobutyl Isobutyrate	198.21		6814	6900	2.442	2.473	+86	+1.3

* In Lossen's paper above alluded to, this value is put=151.7. The determination of Elsässer seems to be even lower than this, and as Schiff lauds very highly the purity of this chemist's investigation materials, it is highly probable that Schiff's own substance in this instance is not as pure as his usually are

† The same remark applies to this also.

TABLE I.—Continued.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma + nb$ + $pc + \dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma + nb + pc + \dots$	per cen age Difference.
Propyl Valerate } $C_8H_{16}O_2$	196.82	6969	6900	2.524	2.499	-69	-1.0
Allyl Acetate } $C_5H_8O_2$	121.5	4520	4500	3.370	3.361	-20	-0.4
Ethyl Oxalate } $C_6H_{10}O_2$	138.79	5108	4950	3.124	3.027	-158	-3.1
Methyl Benzoate } $C_9H_8O_2$	151.65	6653	6600	3.563	3.534	-53	-0.8
Ethyl Benzoate } $C_9H_{10}O_2$	174.65	7335	7350	3.178	3.184	+15	+0.2
Ethyl-oxide } $C_4H_{10}O$	106.27	3441	3600	3.142	3.287	+159	+4.6
Methyl Amyl Ether } $C_6H_{14}O$	148.13	5060	5100	2.807	2.829	+40	+0.8
Paraldehyde } $C_6H_{12}O_3$	150.74	5708	5850	3.084	3.160	+142	+2.5
Acetone } C_3H_6O	77.10	2636	2700	3.894	3.988	+64	+2.4
Valeraldehyde } $C_5H_{10}O$	118.27	4303	4200	3.345	3.265	-106	-2.4
Acetic Anhydride } $C_4H_6O_3$	109.5	4462	4200	3.896	3.666	-262	-5.9
Dimethyl Acetal } $C_4H_{10}O_2$	110.9	4081	4050	3.470	3.443	-31	-0.8
Diethyl Acetal } $C_6H_{14}O_2$	159.91	5444	5550	2.692	2.746	+106	+2.0
Pinacolone } $C_6H_{12}O$	138.25	5017	4950	3.086	3.040	-67	-1.5
Anisol } C_7H_8O	125.21	5503	5550	3.928	3.966	+47	+0.9
Phenetol } $C_8H_{10}O$	149.4	6142	6300	3.370	3.455	+158	+2.5
Methoxycresol ,,	147.8	6345	6300	3.531	3.506	-45	-0.7
Dimethoxy-cresol } $C_8H_{10}O_2$	157.6	7087	7050	3.598	3.582	-37	-0.5
Cuminaldehyde } $C_{10}H_{12}O$	188.9	7750	7700	3.019	3.000	-50	-0.7

TABLE I.—Continued.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma + nb$ $+ pc + \dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma + nb + pc + \dots$	per centage Difference.
Formic Acid } CH_2O_2	41.08	1558	1650	5.917	?	?	?
Acetic Acid } $\text{C}_2\text{H}_4\text{O}_2$	63.40	1853	2400	3.670	?	?	?
Propionic Acid } $\text{C}_3\text{H}_6\text{O}_2$	85.94	2558	3150	3.212	?	?	?
Butyric Acid } $\text{C}_4\text{H}_8\text{O}_2$	108.10	3247	3900	2.886	?	?	?
Isobutyric Acid } " }	109.87	3162	3900	2.746	?	?	?
Valeric Acid } $\text{C}_5\text{H}_{10}\text{O}_2$	130.27	3821	4650	2.570	?	?	?
Ethylene Chloride } $\text{C}_2\text{H}_4\text{Cl}_2$	85.35	3816	3700	4.840	4.692	-116	-3.1
Ethidene Chloride } " }	88.68	3427	3350	4.104	4.012	-77	-2.3
Propyl Chloride } $\text{C}_3\text{H}_7\text{Cl}$	91.58	3263	3425	3.732	3.908	+162	+4.8
Propylene Chloride } $\text{C}_3\text{H}_6\text{Cl}_2$	107.59	4533	4450	4.062	3.988	-83	-1.8
Isobutyl Chloride } $\text{C}_4\text{H}_9\text{Cl}$	114.20	4068	4175	3.333	3.421	+107	+2.6
Isoamyl Chloride } $\text{C}_5\text{H}_{11}\text{Cl}$	134.40	4859	4925	3.118	3.161	+66	+1.4
Chlorobenzene } $\text{C}_6\text{H}_5\text{Cl}$	114.4	5053	5075	4.128	4.146	+22	+0.4
Chlorotoluene } $\text{C}_7\text{H}_7\text{Cl}$	134.9	5848	5825	3.734	3.719	-23	-0.4
Chloroform } CHCl_3	84.65	3443	3450	4.420	4.430	+7	+0.2
Carbontetrachloride } CCl_4	103.77	4313	4300	4.080	4.068	-13	-0.3
Bromine } Br_2	53.52	2792	3000	7.132	7.663	+208	+7.4
Ethyl Bromide } $\text{C}_2\text{H}_5\text{Br}$	77.07	3004	3075	4.443	4.543	+71	+2.3
Ethylene Bromide } $\text{C}_2\text{H}_4\text{Br}_2$	97.01	4900	4500	5.128	4.710	-400	-8.1

TABLE I.—Continued.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma + nb$ + $pc + \dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma + nb + pc + \dots$	per centage Difference
Propyl Bromide } C_3H_7Br	97.05	3830	3825	4.007	4.001	-5	-0.2
Isopropyl Bromide } "	99.2	3814	3825	3.861	3.871	+11	+0.3
Allyl Bromide } C_3H_5Br	90.5	3731	3675	4.334	4.269	-56	-1.5
Isobutyl Bromide } C_4H_9Br	118.39	4613	4575	3.581	3.552	-38	-0.8
Bromo- benzene } C_6H_5Br	119.88	5518	5475	4.204	4.171	-43	-0.8
Bromo- toluene } C_7H_7Br	141.95	6359	6225	3.773	3.694	-134	-2.1
Methyl Iodide } CH_3I	63.9	2864	2975	5.607	5.824	+111	+4.0
Ethyl Iodide C_2H_5I	86.12	3666	3725	4.587	4.661	+59	+1.6
Propyl Iodide } C_3H_7I	106.9	4509	4475	4.080	4.049	-34	-0.8
Isobutyl Iodide } C_4H_9I	128.28	5265	5225	3.624	3.595	-40	-0.8
Isoamyl Iodide } $C_5H_{11}I$	151.05	6000	5975	3.232	3.219	-25	-0.4
Allyl Iodide C_3H_5I	100.9	4415	4325	4.358	4.271	-90	-2.0
Iodobenzene C_6H_5I	130.55	6217	6125	4.168	4.106	-92	-1.5
Propylamine C_3H_7N	85.61	3105	3125	3.920	3.945	+20	+0.6
Allylamine C_3H_7N	78.38	2970	2975	4.290	4.298	+5	+0.2
Isobutyl- amine } $C_4H_{11}N$	106.76	3930	3875	3.563	3.513	-55	-1.4
Diethylamine }	109.05	3795	3875	3.333	3.403	+80	+2.1
Amylamine $C_5H_{13}N$	126.84	4829	4625	3.380	3.238	-204	-4.3
Triethyl- amine } $C_6H_{15}N$	153.82	5259	5375	2.756	2.817	+116	+2.2

TABLE I.—Continued.

Substance.	V Molecular Volume.	$KV^{\frac{2}{3}}$	$ma + nb$ $+ pc + \dots$	K Observed.	K Calculated.	Difference between $KV^{\frac{2}{3}}$ and $ma + nb + pc + \dots$	per centage Difference.
Aniline C_6H_7N	106.08	5168	5075	4.730	4.645	-93	-1.8
Pyridene C_5H_5N	89.39	4137	4325	4.895	5.116	+188	+4.5
Piperidene $C_5H_{11}N$	108.76	4693	4775	4.138	4.208	+82	+1.7
Quinoline C_9H_7N	139.75	7355	7175*	4.452	4.343	-180	-2.4
Nitro- methane } CH_3NO_2	59.5	2390	2375	5.207	5.175	-15	-0.6
Nitroethane $C_2H_5NO_2$	80.25	3070	3125	4.271	4.347	+55	+1.7
Isoamyl- nitrate } $C_5H_{11}NO_3$	152.59	5923	5825	3.142	3.091	-98	-1.6
Acetonitrile C_2H_3N	57.23	1873	1875	4.327	4.331	+2	+0.1
Propionitrile C_3H_5N	78.28	2649	2625	3.825	3.790	-24	-0.8
Capronitrile $C_6H_{11}N$	141.1	5345	4875	3.189	2.909	-470	-9.0
Ethyl Sulphide } $C_4H_{10}S$	122.2	4622	4650	3.420	3.440	+28	+0.6
Allyl Thio- carbimide } C_4H_5NS	123.13	5046	4925	4.193	4.092	-121	-2.4
Phenyl thio- carbimide } C_7H_5NS	143.7	7021	7025	4.077	4.081	+4	+0.05
Methyl thio- cyanate } C_2H_3NS	78.96	3329	3375	4.745	4.816	+46	+1.5
Ethyl thio- cyanate } C_3H_5NS	99.84	4166	4125	4.176	4.135	-41	-1.0
Carbon Bisulphide } CS_2	62.06	2842	2900	5.813	5.930	+58	+2.0

* $9 \times 600 + 7 \times 75 + 650 = 6575$ $6575 + 2 \times 300 = 7175$. But this mode of calculation is probably incorrect.

The Atomic constants (*a' b' c'*) for the various elements used in the calculation of the second table are as follows:

- for carbon 44 when there is no double linking.
 „ hydrogen 21.5 in all cases.
 „ oxygen 31 in alcohols.
 „ „ 44 when combined with two carbon atoms.
 „ „ 55 when connecting a carbon atom to a benzene ring.
 „ chlorine 119 when only one atom of chlorine is united with a carbon atom.
 „ chlorine 110 when two or more atoms of chlorine are united with a carbon atom.
 „ bromine 162 when only one atom of bromine is united with a carbon atom.
 „ iodine 215 when only one atom of iodine is united with a carbon atom.
 „ nitrogen 54 in all cases where it is a triad.
 „ sulphur 148 when combined with two carbon atoms.

When two atoms are united together by more than one bond, the value of $K^{\frac{1}{2}}V^{111}$ is increased by 19 for each additional bond.

Thus :

$$\text{group } (\text{>C=C<}) = 107 = 2 \times 44 + 19$$

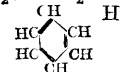
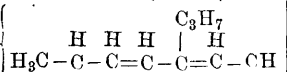
$$\text{group } (\text{>C=O}) = 118 = 44 + 55 + 19$$

$$\text{group } (-C \equiv N) = 136 = 44 + 54 + 2 \times 19$$

$$\text{group } (-N=C=S) = 284 = 44 + 54 + 19 + 148 + 19$$

$$\left. \begin{array}{l} \text{group } (SCN) = 270 \\ \text{group } (NO_2) = 172 \end{array} \right\} \text{these have not been resolved.}$$

TABLE II.

Substance.	<i>K</i> .	\bar{V} Molecular Volume.	$K^{\frac{1}{3}}\bar{V}^{1.18}$.	$ma' + nb'$ + $pc' + \dots$	Difference between $K^{\frac{1}{3}}\bar{V}^{1.18}$ and $ma + nb + pc + \dots$	per centage Difference.
Normal Hexane C_6H_{14}	2.772	140.02	567	565	- 2	-0.35
Normal Heptane C_7H_{16}	2.575	162.56	652	652	± 0	± 0.00
Diisobutyl $(C_4H_9)_2$	2.410	184.89	734	739	+ 5	+0.68
Diisoamyl $(C_5H_{11})_2$	2.192	231.80	915	913	- 2	-0.22
Amylene C_5H_{10}	3.082	110.18	451	454	+ 3	+0.66
Octylene C_8H_{16}	2.572	177.61	723	715	- 8	-1.11
Diallyl $H_2C=C(H)-CH_2-C(H)=CH_2$	3.008	126.10	521	517	- 4	-0.77
Benzene 	4.254	96.17	451	450	- 1	-0.22
Toluene $HC=C(H)-C(H)=C(H)-CH_3$	3.692	118.25	536	537	+ 1	+0.19
Xylene (1 : 2) C_8H_{10}	3.354	139.91	624	624	± 0	± 0.00
„ (1 : 3) „	3.358	139.69	623	624	+ 1	+0.16
„ (1 : 4) „	3.340	140.21	624	624	± 0	± 0.00
Ethyl Benzene $C_6H_5.C_2H_5$	3.420	138.96	624	624	± 0	± 0.00
Propyl Benzene $C_6H_5.C_3H_7$	3.122	161.82	714	711	- 3	-0.42
Ethyl Toluene $C_6H_4.CH_3.C_2H_5$	3.092	161.95	712	711	- 1	-0.14
Mesitylene (1 : 3 : 5) $C_6H_3(CH_3)_3$	3.012	162.41	705	711	+ 6	+0.85
Cymene (1 : 5) $C_6H_4(CH_3)(C_3H_7)$	2.782	184.46	787	798	+11	+1.40
Terpene (citrene) 	2.748	186.3 *	791	822	+31	+4.

* For the peculiarity of the molecular volume of this compound, see the foot-note annexed to the foregoing table.

TABLE II.—Continued.

Substance.	K .	V Molecular Volume.	$K^{\frac{2}{3}}v_{118}$.	$ma' + nb'$ $+ pc' + \dots\dots$	Difference between $K^{\frac{2}{3}}v_{118}$ and $ma + nb + pc + \dots\dots$	per centage Difference.
Terpene (citrene) $\left\{ \begin{array}{c} \text{H} \text{ H} \text{ H} \text{ C}_3\text{H}_7 \\ \quad \quad \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}=\text{C}-\text{C}=\text{C}-\text{CH}_2 \end{array} \right.$	2.624	196.	819	822	+ 3	+0.37
Methyl Alcohol CH_3OH	3.818	42.72	164	161	- 3	-1.83
Ethyl Alcohol $\text{C}_2\text{H}_5\text{OH}$	3.530	62.19	246	248	+ 2	+0.81
Propyl Alcohol $\text{C}_3\text{H}_7\text{OH}$	3.524	81.29	337	335	- 2	-0.59
Isopropyl Alcohol $(\text{C}_3\text{H}_7)^{\beta}\text{OH}$	3.404	81.69	333	335	+ 2	+0.60
Isobutyl Alcohol $(\text{C}_4\text{H}_9)^{\beta}\text{OH}$	3.208	101.64	418	422	+ 4	+0.95
Isoamyl Alcohol $(\text{C}_5\text{H}_{11})^{\beta}\text{OH}$	3.068	122.74	511	509	- 2	-0.40
Dimethyl Ethyl Carbinol $\left\{ \text{C}_5\text{H}_{12}\text{O} \right.$	3.100	121.27	506	509	+ 3	+0.60
Allyl Alcohol $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$	3.910	74.11	318	311	- 7	-2.20
Methyl Formate HCO_2CH_3	4.944	62.65	293	292	- 1	-0.34
Ethyl Formate $\text{HCO}_2\text{C}_2\text{H}_5$	3.952	84.57	374	379	+ 5	+1.34
Methyl Acetate $\text{H}_3\text{C}_2\text{O}_2\text{CH}_3$	4.020	83.66	372	379	+ 7	+1.88
Propyl Formate $\text{HCO}_2\text{C}_3\text{H}_7$	3.710	106.15	474	466	- 8	-1.68
Ethyl Acetate $\text{H}_3\text{C}_2\text{O}_2\text{C}_2\text{H}_5$	3.542	105.78	461	466	+ 5	+1.08
Methyl Propionate $\text{H}_5\text{C}_3\text{O}_2\text{CH}_3$	3.612	104.27	457	466	+ 9	+1.97
Isobutyl Formate $\text{HCO}_2(\text{C}_4\text{H}_9)^{\beta}$	3.230	130.74	565	553	-12	-2.12
Propyl Acetate $\text{H}_3\text{C}_2\text{O}_2\text{C}_3\text{H}_7$	3.184	128.56	550	553	+ 3	+0.60
Ethyl Propionate $\text{H}_5\text{C}_3\text{O}_2\text{C}_2\text{H}_5$	3.168	127.86	545	553	+ 8	+1.45
Methyl Butyrate $\text{H}_7\text{C}_4\text{O}_2\text{CH}_3$	3.250	126.36	544	553	+ 9	+1.65

TABLE II.—Continued.

Substance.	K.	V Molecular Volume.	$K^{\frac{1}{3}}$ plus.	$mc' + nd'$ + $pe' + \dots$	Difference between $K^{\frac{1}{3}}$ plus and $mc' + nd' + pe' + \dots$	per centage Difference.
Methyl Isobutyrate ($H_7C_4O_2$) ^a CH ₃	3.190	126.44	540	553	+13	+2.41
Isoamyl Formate HCO ₂ (C ₅ H ₁₁) ^b	3.080	153.22	665	640	-25	-3.76
Isobutyl Acetate H ₃ C ₂ O ₂ (C ₄ H ₉) ^b	2.978	152.51	651	640	-11	-1.69
Propyl Propionate H ₅ C ₃ O ₂ C ₃ H ₇	2.922	150.70	635	640	+ 5	+0.79
Ethyl Butyrate H ₇ C ₄ O ₂ C ₂ H ₅	2.908	150.25	632	640	+ 8	+1.27
Ethyl Isobutyrate ($H_7C_4O_2$) ^a C ₂ H ₅	2.836	150.68	626	640	+14	+2.23
Methyl Valerate H ₉ C ₅ O ₂ CH ₃	3.006	148.33	632	640	+ 8	+1.27
Isoamyl Acetate H ₃ C ₂ O ₂ (C ₅ H ₁₁) ^c	2.762	174.60	735	727	- 8	-1.09
Isobutyl propionate H ₅ C ₃ O ₂ (C ₄ H ₉) ^b	2.648	173.55	714	727	+13	+1.82
Propyl Butyrate H ₇ C ₄ O ₂ C ₃ H ₇	2.700	173.85	723	727	+ 4	+0.55
Propyl Isobutyrate ($H_7C_4O_2$) ^b C ₃ H ₇	2.634	174.20	716	727	+11	+1.54
Ethyl Valerate (H ₉ C ₅ O ₂)C ₂ H ₅	2.698	172.99	718	727	+ 9	+1.25
Isoamyl Propionate H ₅ C ₃ O ₂ C ₅ H ₁₁	2.524	195.96	810	814	+ 4	+0.49
Isobutyl Butyrate H ₇ C ₄ O ₂ (C ₄ H ₉) ^b	2.442	197.65	800	814	+14	+1.73
Isobutyl Isobutyrate } ($H_7C_4O_2$) ^b (C ₄ H ₉) ^c	2.442	198.21	803	814	+11	+1.38
Propyl Valerate H ₉ C ₅ O ₂ C ₃ H ₇	2.524	196.82	809	814	+ 5	+0.62
Allyl Acetate H ₅ C ₂ O ₂ C ₃ H ₅	3.370	121.5	529	529	± 0	±0.00
Ethyl Oxalate C ₂ O ₄ (C ₂ H ₅) ₂	3.124	138.79	739	716	-23	-3.11
Methyl Benzoate C ₇ H ₅ O ₂ CH ₃	3.553	151.65	707	699	- 8	-1.13
Ethyl Benzoate C ₇ H ₅ O ₂ C ₂ H ₅	3.178	174.65	789	786	- 3	-0.38

TABLE II.—Continued.

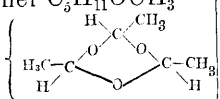
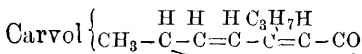
Substance.	K.	V Molecular Volume.	$K^{\frac{2}{3}}V^{1.18}$.	$ma' + nb' + pc' + \dots$	Difference between $K^{\frac{2}{3}}V^{1.18}$ and $ma + nb + pc + \dots$	per centage Difference.
Ethyl Oxide $(C_2H_5)_2O$	3.142	106.27	436	435	- 1	-0.23
Methyl Amyl Ether $C_5H_{11}OCH_3$	2.807	148.13	610	609	- 1	-0.16
Paraldehyde 	3.084	150.74	654	654	± 0	± 0.00
Dimethyl Acetal $\begin{cases} H_2=C-O-CH_3 \\ H_2=C-O-CH_3 \end{cases}$	3.470	110.9	484	480	- 4	-0.83
Diethyl Acetal $\begin{cases} H_2=C-O-C_2H_5 \\ H_2=C-O-C_2H_5 \end{cases}$	2.692	159.91	654	653	- 1	-0.15
Acetone $H_3C-CO-CH_3$	3.894	77.10	333	335	+ 2	+0.60
Valeraldehyde $C_5H_{10}O$	3.345	118.27	511	509	- 2	-0.39
Pinacolone $(CH_3)_3CO.CH_3$	3.086	138.25	591	596	+ 5	+0.84
Acetic Anhydride $(C_2H_3O)_2O$	3.896	109.5	503	498	- 5	-0.99
Anisol $C_6H_5OCH_3$	3.928	125.21	592	592	± 0	± 0.00
Phenetol $C_6H_5OC_2H_5$	3.370	149.4	675	679	+ 4	+0.59
Methoxycresol $C_6H_4(OCH_3)CH_3$	3.531	147.8	683	679	- 4	-0.58
Dimethoxycresol $C_6H_4(OCH_3)_2$	3.598	157.6	741	734	- 7	-0.95
Cuminaldehyde $(CH_3)_2CH.C_6H_4CHO$	3.019	188.9	837	829	- 8	-0.95
Carvol 	3.169	190.26	872	853	-19	-2.18
Formic Acid $HCOOH$	5.917	41.08	195	205	?	

TABLE II.—Continued.

Substance.		K.	V Molecular Volume.	$K^{\frac{1}{2}}V^{1/3}$.	$\frac{ma+nb}{+pc+.....}$	Difference between $\frac{K^{\frac{1}{2}}V^{1/3}}$ and $\frac{ma+nb}{+pc+.....}$	per centage Difference.
Acetic Acid	$C_2H_4O_2$	3.670	63.40	256	292	?	
Propionic Acid	$C_3H_6O_2$	3.212	85.94	343	379	?	
Butyric Acid	$C_4H_8O_2$	2.886	108.10	427	466	?	
Isobutyric Acid	„	2.746	109.87	424	466	?	
Valeric Acid	$C_5H_{10}O_2$	2.570	130.27	502	553	?	
Ethylene Chloride	$(CH_2Cl)_2$	4.840	85.35	418	412	- 6	-1.44
Ethidene Chloride	$H_3C-CHCl_2$	4.104	88.68	403	394	- 9	-2.23
Propyl Chloride	C_3H_7Cl	3.732	91.58	399	402	+ 3	+0.75
Propylene Chloride	$C_3H_6Cl_2$	4.062	107.59	503	499	- 4	-0.79
Isobutyl Chloride	$(C_4H_9)^{\beta}Cl$	3.333	114.20	489	489	± 0	± 0.00
Isoamyl Chloride	$(C_5H_{11})^{\gamma}Cl$	3.118	134.40	573	576	+ 3	+0.52
Chlorobenzene	C_6H_5Cl	4.128	114.4	546	548	+ 2	+0.37
Chlorotoluene	$H_3C.C_6H_4Cl$	3.734	134.9	630	635	+ 5	+0.79
Chloroform	$CHCl_3$	4.420	84.65	396	396	± 0	± 0.00
Carbon Tetrachloride	$\left. \begin{array}{l} \\ \end{array} \right\} CCl_4$	4.080	103.77	483	484	+ 1	+0.21
Bromine	Br_2	7.132	53.52	293	—	?	?
Ethyl Bromide	C_2H_5Br	4.443	77.07	355	358	+ 3	+0.84
Ethylene Bromide	$(CH_2Br)_2$	5.128	97.01	501	499	- 2	-0.40

TABLE II.—Continued.

Substance.	K.	Γ Molecular Volume.	$K^{\frac{1}{3}}\Gamma^{1/3}$.	$ma + nb$ + $pc' + \dots$	Difference between $K^{\frac{1}{3}}\Gamma^{1/3}$ and $ma + nb + pc' + \dots$	per centage Difference.
Propyl Bromide C_3H_7Br	4.007	97.05	443	445	+ 2	+0.45
Isopropyl Bromide $(C_3H_7)^{\beta}Br$	3.851	99.2	446	445	- 1	-0.23
Allyl Bromide C_3H_5Br	4.334	90.5	424	420	- 4	-0.94
Isobutyl Bromide $(C_4H_9)^{\beta}Br$	3.581	118.39	529	531	+ 2	+0.38
Bromobenzene C_6H_5Br	4.204	119.88	582	580	- 2	-0.35
Bromotoluene $H_3C.C_6H_4Br$	3.773	141.95	671	667	- 4	-0.59
Methyl Iodide CH_3I	5.607	63.9	320	324	+ 4	+1.25
Ethyl Iodide C_2H_5I	4.587	86.12	411	411	± 0	± 0.00
Propyl Iodide C_3H_7I	4.080	106.9	501	498	- 3	-0.60
Isobutyl Iodide $(C_4H_9)^{\beta}I$	3.624	128.28	585	585	± 0	± 0.00
Isoamyl Iodide $(C_5H_{11})^{\beta}I$	3.232	151.05	670	672	+ 2	+0.30
Allyl Iodide $\left\{ \begin{array}{l} H \quad H_2 \\ H_2C=C-CI \end{array} \right.$	4.358	100.9	483	474	- 9	-1.86
Iodobenzene C_6H_5I	4.168	130.55	641	644	+ 3	+0.47
Propylamine $C_3H_7.NH_2$	3.920	85.61	378	380	+ 2	+0.53
Allylamine $C_3H_5NH_2$	4.290	78.38	356	356	± 0	± 0.00
Isobutylamine $(C_4H_9)^{\beta}NH_2$	3.563	106.76	467	467	± 0	± 0.00
Diethylamine $(C_2H_5)_2NH$	3.333	109.05	463	467	+ 4	+0.86
Triethylamine $(C_2H_5)_3N$	2.756	153.82	632	641	+ 9	+1.42
Aniline $C_6H_5NH_2$	4.730	106.08	533	526	- 7	-1.31

TABLE II.—Continued.

Substance.	K .	V Molecular Volume.	$K^{\frac{1}{3}}V^{1.18}$.	$ma' + nb'$ $+ pc' + \dots\dots\dots$	Difference between $K^{\frac{1}{3}}V^{1.18}$ and $ma + nb$ $\epsilon + \dots\dots\dots$	per centage Difference.
Water H_2O	11.935*	18.74	110	98	?	

The average difference between the observed and the calculated values of $KV^{\frac{3}{2}}$, and therefore of K , in the first table is $\pm 1.85\%$; while the similar difference in the values of $K^{\frac{1}{3}}V^{1.18}$ in the second table is not more than 0.90% , the agreement being much closer. The value of K calculated therefrom is, however, again about the same as that in the first table, viz., 1.8% .

These results are more satisfactory than those obtained by Schiff's formula, which gives values of N differing from the observed values by 3.5% on the average; and as N is proportional to K , it may be observed that the average difference between the experimental and the calculated values of K according to the formulæ here proposed is only one-half of the similar difference which obtains between the values of N when Schiff's formula is employed. In the first table there are four instances of great discrepancies, ranging from 7.4 to 9.0% . Of these, isoamyl-formate has an exceptionally large value for K , it being about 6% higher than the average value of four of its isomers, while its molecular volume given by Schiff seems to be too high by two per cent., so that there is some reason to believe that a careful redetermination of these data might remove this discrepancy. The next case is bromine, of which it is sufficient to remark that this element might possibly have two capillary constants as its brother

* This is calculated from Frankenheim's determination.

element chlorine, whose lower value applies to the cases where two or more atoms of chlorine are closely united together. Of the remaining two abnormal cases, ethylenedibromide and capronitrile, I have no remark to offer. They must be looked upon as genuine exceptions. In the second table the discrepancies are much smaller except in the case of bromine, but the remark made above about this element applies here also. The acids form an important group of exceptions in both tables as well as in Schiff's paper; this is probably owing to the abnormality of their molecular magnitude at the boiling points, and it would be strange indeed if the capillary phenomena did not show an analogous abnormality.

The atomic capillary constants above given must be regarded as only rough approximations. The values for carbon, hydrogen, chlorine, bromine, iodine, &c.....in the first table may be higher or lower than the true values by 50 units, while the difference may be greater in other elements. The values of atomic capillary constants used in the calculation of the second table seem to be much closer to the true values, and may be assumed to be correct within 5 units. A better determination of these constants, or a better choice of the coefficient of V , may give much better results than have been obtained from the calculations given above.

The first formula can be applied to the approximate determination of the molecular magnitude of a liquid compound, provided its percentage composition as well as the probable nature of its atomic concatenation, the capillary height (h) for a tube of known internal perimeter at the boiling point, and the specific gravity (ρ) at the same temperature are known. Suppose the empirical formula of the liquid to be $A_{m'} B_{n'} C_{p'} \dots \dots \dots$, where m' , n' , p' ,..... may be integral or fractional; put this mass= M and divide it by ρ , and designate the quotient by V' . Further, suppose the true molecular mass= xM .

Then by the formula we have

$$h\rho = K = \frac{x(m'a + n'b + p'c + \dots)}{x^{\frac{3}{2}}V'^{\frac{3}{2}}}. \quad \text{Hence } x^{\frac{1}{2}} = \frac{m'a + n'b + p'c + \dots}{KV'^{\frac{3}{2}}}$$

$$\text{or } x = \frac{(m'a + n'b + p'c + \dots)^2}{K^2V'^3}.$$

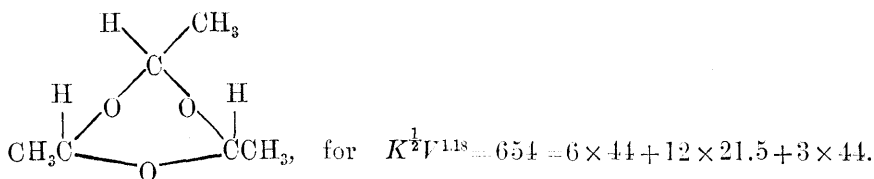
For example, toluene contains 91.3 % of carbon and 8.7 % of hydrogen ; dividing the one by 11.97, and the other by unity, we get the empirical formula $C_{7.63}H_{8.7} = M = 100$. The specific gravity at the boiling point is 0.776, so that $V' = 128.8$ and the observed value of K is 3.692. Substituting these values in the above formula we have

$$x = \frac{(7.63 \times 600 + 8.7 \times 75)^2}{(3.692)^2 \times (128.8)^3} = .939.$$

Therefore, the molecular magnitude is $C_{7.63 \times .939}H_{8.7 \times .939} = C_{7.14}H_{8.16}$. This result is too high by 2 %, inasmuch as the calculated and the observed values of K show a difference of 1.1 %. If this difference be 2 % as it is most likely to be, then the molecular magnitude would differ by 4 %, which may be regarded as fairly approximate. But whenever this mode of determining molecular magnitude is applicable, the vapor density method can also be employed, so that this application of capillary determination is more curious than useful.

The second formula seems to be of greater interest to chemists, for it shows the close relationship between the mode of atomic linking and the capillary phenomena. It can be applied with caution to determine the number of double bonds in carbon compounds, for whenever there is one the value of $K^{\frac{1}{2}}V'^{1.18}$ is increased by about 19 units, which is quite a large quantity compared with the probable discrepancy between the observed and the calculated values of $K^{\frac{1}{2}}V'^{1.18}$. Benzene has three double bonds according to this mode of calculation, while allyl compounds seem to have only one such bond. This is in accordance with the conclusion of Bruhl from optical determination.

In the case of terpene, if we assume $V=196$, then the result agrees with Bruhl's investigation, but if $V=186.3$ then there can be no double bond, or at most only one. Quinoline has only five double bonds according to the accepted formula, while the calculation from the capillary height indicates six such linkings. Carvol also shows a similar peculiarity. The capillary value of the oxygen atom varies in a very peculiar manner; in alcohols it is only 31, in ethers and acetals it is 44, while it attains its seemingly normal value in aromatic compounds where it is 55. In aldehydes and acetones it is $74=55+19$. The calculation according to this formula seems to justify the commonly accepted constitution of paraldehyde



It may be objected that the value for the group $\langle \text{C}=\text{C} \rangle = 107$ has been obtained by making the value for hydrogen too high, and that the conclusion about the atomic linking arrived at in this way is not trustworthy. But the agreement between the observed and the calculated values of $K^{\frac{1}{2}}V^{1.18}$ for piperidene which has no double bond, but which has two atoms of hydrogen less than what a saturated compound ought to have, seems to prove the correctness of the above conclusion. When well worked out the capillary phenomena are likely to afford some insight into the atomic grouping of a molecule, but this can not be attempted with confidence until more accurate data are amassed.

So far the claim of the formulæ seems to be fairly made out, still there are many grave considerations which tend to show that the connections expressed by the equations are more accidental than

essential, and warn us not to theorize too freely from any such hasty generalization. That there are more than one formulæ, which have no essential relation to each other, to express one and the same connection, seems in itself to be a strong proof of their being of an accidental nature. A thing (A) may depend entirely on another (B); but if (B) can influence a third (C), or is always (or even usually) accompanied by it, then the proposition connecting (A) and (C) will sometimes have the appearance of a law. If it holds good for a great number of instances, then it may be assumed to be true within certain limits, and can be used as a sort of a law, though theoretically it is not. Just as, in using a circle of a certain radius to represent a short piece of almost any curve, we must assign a strict limit to the length of the substituted arc lest the error grow inadmissively large; so here, these accidental laws must not be stretched too far. The formulæ developed in this paper do not apply to the case of water. This may be owing to the fact that water has a very small molecular magnitude compared with the substances treated of in this paper, so that it does not lie within the limit of applicability of the formulæ. Or it may be due to the fact that water has a critical temperature so abnormally high that it is not comparable with other substances at the temperature at which the vapor pressure is equal to a certain fixed quantity. Or it may be due to some unknown cause, as is the case with the magnetic rotation of light, where water has a far greater value than can be inferred from its composition. But one thing is certain that this abnormally high capillary constant for water is not due to the complexity of its molecular structure, for the larger the molecule, the less must be the capillary attraction, supposing the formulæ to be true. This difficulty can, of course, be eluded by giving oxygen combined with two hydrogen atoms a certain arbitrary value, so as to make the calculated value of K agree with the observed. This,

however, is begging the whole question, for there is no other compound with which to test the validity of this particular value. Schiff's formula is far better than the new ones in this instance, for the extrapolated value of N for water seems to agree tolerably well with the actual value.

The next thing to be considered is the mode of measuring the constant. The capillary height multiplied by the specific gravity and divided by 2 does not represent the capillary constant or the surface tension; for according to the theory of capillary attraction $\rho V = Tl \cos i$ or $V = a^2 l \cos i$, where V is the volume of the liquid raised in the tube, ρ is the density, l the internal perimeter of the tube, T the surface tension, a^2 the capillary constant, i the contact angle. When a circular tube is used as in the experiment of Schiff and most other investigators, $l (= 2\pi r)$ might be measured with fair approximation; V can also be found out with tolerable accuracy, but it is next to an impossibility to measure i in the tube method. As has been criticized by Volkmann, Schiff made an unwarrantable assumption that i is always zero in the liquids investigated by him, and calculated out a^2 accordingly. But as the value of i in the various liquids investigated by Schiff appears to be pretty large, especially in the case of chloroform, what he calls the capillary constant of a substance at the boiling point cannot be accepted as such indiscriminately; and the more so, since, as he himself points out, i changes with rise of temperature, and since the boiling points of many liquids given in his communications are somewhat high, i cannot be zero even where it is so at ordinary temperatures. Volkmann has calculated the value of i for all the liquids contained in the first communication of Schiff's, from the height of the meniscus given in the paper. But, as Schiff replies, the meniscus height is undoubtedly one of the most difficult of quantities to measure. Indeed, the recalculation made by Volkmann

cannot be looked upon as an improvement, for according to it the value of i for hydrocarbons is sometimes very considerable, while that for chloroform is very small. Empirically, Schiff's work is of great value, for whatever may be the value of i , the capillary height h is a well defined quantity and can be accurately measured, and the relation found between capillary height and chemical composition is valid whether the constant is theoretically correct or not. Still from a strictly scientific point of view, the investigation must be deemed very imperfect, involving, as it does, an incorrect method of calculation. It is, therefore, very desirable that the matter should be investigated anew with an entirely different method, if possible, so as to confirm Schiff's work, and to remove all inaccuracies as far as practicable. The tube method is said to be the most accurate, still there is the drawback above alluded to. The plate and bubble method of Quincke is theoretically good, but practically the results obtained are but rough approximations. The drop method is not well fitted for accurate determinations, and the same may be said of the contact plate method which has been employed, amongst others by Schall, for similar purposes. The ring method used by Duprè and Wilhelmi has been taken up by Prof. Yamagawa of the Imperial University, who has given an expression by which the error due to hydrostatic pressure may be eliminated, and which has been applied to the measurement of surface tensions of various liquids. Timbery* has used a thin platinum ring to investigate the influence of temperature on capillary constants. He gives only one determination by this method for each temperature, while he takes the average of several measurements by Quincke's method. He says that the result obtained by the former method is so accurate and certain that no second determination is required to confirm it. This is an excellent account, and my own experience

* Wiedemann's Annalen 30 (1887) s.545.

fully corroborates it. When a ring with a very thin edge is used, the configuration for maximum surface-tension is most probably attained when $i=0$, so that the correction for the contact angle is not required. I have tested a few liquids by this method with a very thin circular platinum ring, and have obtained the following results :

	Traction on the Ring		Capillary Height \times Specific Gravity		Contact Angle Temperature 27°–28°.
	in grammes.	Water=1.000.	No. of thermometer Grade \times Sp. Gr.	Water=1.000.	
Water	1.668	1.000	136.8	1.000	Supposed to be zero.
Alcohol	.526	.315	42.5	.311	„
Chloroform	.6215	.373	48.4	.357	18°
Benzene	.6535	.392	45.1	.395	Supposed to be zero.

These are but rough determinations, the substances used being only tolerably pure ; still the difference between the results obtained by the tube method and by the ring method is very significant. The capillary tube used in these experiments was a broken thermometer of a good bore, which showed no difference in the length of a mercury thread about the places used for the measurements. As the bore is very small (about $\frac{1}{8}$ of a millimetre), no correction has been made for the meniscus. The ring had a perimetre of 69.8 m.m., and as it was very thin no correction has been made for hydrostatic pressure. The contact angle of benzene seems to be zero, while that of chloroform is rather large. It seems, therefore, advisable to use this method of measuring surface tension. As air is said to have considerable influence in depressing the capillary height in the case of water, it is desirable to conduct the experiment in vacuum, and as organic liquids dissolve gases with greater readiness than water does, the error

from this source may be considerable.* The second series of Schiff's experiments is reported to be free from this source of inaccuracy.

Another consideration which tends to diminish the value of the formulæ is the temperature of comparison. The choice of the boiling points seems to be rather arbitrary, the pressure of vapor chosen depending entirely on the accident of our habitation. The theories of Van der Waal may perhaps give some aid in determining the temperature of comparison, but it is also probable that it will not furnish very accurate guidance. The only way to do this properly is to investigate the influence of temperature on capillary phenomena by a thoroughly reliable method, to see whether it has any relation to the changes of density of the liquid and pressure of the vapor and other concomitant phenomena.

All these considerations take away much of the apparent value of Schiff's formula as well as of those proposed in this paper, and call for a new and accurate investigation of the phenomena. The physical properties of all substances must chiefly depend on the chemical composition, and the science of chemistry must be regarded as being grievously backward, so long as she cannot predict these properties from the knowlege of the chemical constitution.

In conclusion I have to return my best thanks to Professor J. Sakurai, for the great interest which he has taken in my work and for his valuable suggestions.



* But this inaccuracy may be disguised by the smallness of the capillary constants in organic liquids.