XIX. *On Liquid Transpiration in relation to Chemical Composition.*

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The passage of liquids under pressure through a capillary tube is here spoken of as liquid transpiration, in accordance with the analogy of gaseous transpiration. The subject owes the development which it has already acquired chiefly to the investigations of the late Dr. Poiseuille*. The precision of the results attainable by the mode of experimenting pursued by that physicist has been remarked on by every one who has followed him in the inquiry. The observations we owe to M. Poiseuille and other inquirers are very numerous, but have not, so far as I am aware, been connected hitherto with any speculative views of the chemical or molecular constitution of liquids.

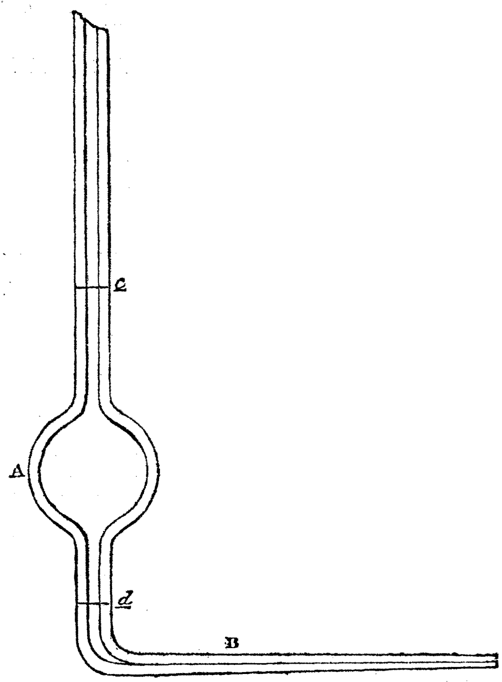
The isolated discovery of M. Poiseuille, that diluted alcohol has a point of maximum retardation, coinciding with the degree of dilution at which the greatest condensation of the mixed liquids occurs, appears to offer a starting-point for new inquiries. The same result may be otherwise expressed, by saying that the definite compound of 1 equiv. of alcohol with 6 equivs. of water, $C_4 H_6 O_2 + 6 HO$†, is more retarded than alcohol containing either a greater or a smaller proportion of water. The rate of transpiration appears here to depend upon chemical composition, and to afford an indication of it. A new physical property may thus become available for the determination of the chemical constitution of substances. Methylic alcohol being found to exhibit the same remarkable feature in its transpiration, although the 6-hydrate of that alcohol is not distinguished by extraordinary condensation of volume, the inquiry was extended to the hydrated acids. The results obtained with the latter substances give a certain degree of generality to the relation subsisting between the transpirability and chemical composition of liquids.

The apparatus employed was very similar to that of M. Poiseuille. It consisted of a small but rather stout glass bulb, A (see figure), about two-thirds of an inch in diameter, having a capacity of from 4 to 8 cub. cent., blown upon a thick glass tube, with a bore of about 2 millimetres. A scratch (*c*) was made upon the glass tube above, and another (*d*) below the bulb, to indicate the available capacity of the instrument. The lower tube was bent at a right angle to the upper, and a fine capillary tube, B, from 3 to 4 inches in length, was sealed to the curved extremity of the tube. The bulb and capillary were always held immersed in a vessel of water during the experiment, in order to secure uniformity of temperature. The force employed to impel the liquid through the

* Mém. Savans Étrangers, tom. ix. p. 433.

† Halving the equivalent of alcohol, the hydrate of greatest retardation becomes $C_2 H_3 O + 3 HO$.

capillary was the weight of one atmosphere of 760 millimetres of mercury, and was obtained from compressed air contained in a large reservoir provided with a mercurial gauge, as in POISEUILLE'S experiments. The time was noted in seconds which the level of the liquid in the bulb took to fall from the mark *c* to the mark *d*. This time varied from about 300 to 900 seconds in different liquids. In successive experiments made upon the same liquid, the variation in the time, or error of observation, did not exceed one or two seconds. The experiment was always repeated two or three times, and a mean taken. The temperature of the liquid transpired was 20° (68° F.), when not otherwise stated.



The liquid may be introduced into the bulb through the open upper tube by means of a tube-funnel; but it was found more convenient in practice, although requiring a much longer time, to fill the bulb by aspiration through the capillary. With this view the compressed air was shut off by a stop-cock, and the upper tube of the bulb was then allowed to communicate with the receiver of an air-pump, instead, by which exhaustion was produced, while the open end of the capillary was immersed in a portion of the liquid. The liquid which entered the bulb in this manner was sure to be free from any solid matter which could cause obstruction in the capillary during the subsequent passage of the liquid outwards, while the disconnecting of the bulb from the rest of the apparatus, for the purpose of filling the former, was also avoided.

Nitric Acid.

A bulb provided with a capillary tube, distinguished as capillary C, was used in the transpiration of nitric acid and of several other liquids. The dimensions of this bulb C were as follows:—Capacity of bulb, 8·075 cub. cent.; length of capillary tube, 28 millims.; diameter of bore, 0·0942 millim. The time of passage of water through the tube, under the pressure of one atmosphere and at the fixed temperature of 20°, was 348 seconds. The time of the passage of the most highly concentrated nitric acid through the same capillary was found to be 344·5 seconds, or slightly less than the time of water. This is the protohydrate of nitric acid, $HO.NO_5$ or NHO_6. With the addition of water to the acid, the transpiration of equal volumes of liquid becomes gradually slower; till as much as three additional equivalents of water were added, when the transpiration-time rose to its maximum, 732 seconds. The last hydrate is the well-known definite compound NHO_6+3HO, having the specific gravity 1·4, and which possesses the highest boiling-point of any compound of nitric acid and water. Diluted beyond this point nitric acid begins to pass more freely, and the transpiration-time approaches again to that of water. With the addition of twice its weight of water, or about 7 equivalents, the acid passed through the capillary in 472 seconds.

The experiments made upon nitric acid are recorded in the following Table. It will be observed that the retardation is considerable for a certain distance on both sides of the maximum point. No unusual retardation appears to occur with the proportions of water corresponding to 2 and 4 equivalents. The specific gravity of the acid liquid is added in the last column of the Table, whenever that property was observed.

TABLE I.—Transpiration of Nitric Acid, at 20° C., by Capillary C*.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (NHO_6).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water=1.	
0	0	344·5	0·9899	1·5046
25·47	20·38	692	1·9885	1·4358
28·56 ... 2 eqs. HO	21·43	705	2·0258	
30	23·07	712	2·0459	
40	28·50	725	2·0833	
42·85 ... 3 eqs. HO	29·99	732	2·1034	1·3978
45	31·03	730	2·0977	
50	33·33	728·5	2·0919	1·3816
55	35·48	718	2·0632	
57·12 ... 4 eqs. HO	36·35	712	2·0459	
60	37·50	709·5	2·0387	1·3598
70	41·17	683	1·9626	1·3407
80	44·44	661	1·8994	1·3239
90	47·36	635·5	1·8261	
100	50·00	593	1·7040	1·2943
200	66·66	472	1·3563	

It appears, then, that a certain hydrate of nitric acid is marked out by its low transpirability so distinctly, that nitric acid could be identified by that physical property. Such a property may prove to be typical of a class of acids to which nitric acid belongs. The hydration of nitric acid probably advances by three equivalents at a time, NHO_6+3HO, as it does in the magnesian nitrates, $NMO_6+3HO+3HO$. The transpiration of the assumed second hydrate of nitric acid was not made the subject of experiment. A certain steadiness is observed in the transpiration of this acid on either side of the point of maximum retardation.

* In the following Tables, the particular capillary employed is in each case designated by a particular letter. Capillary C, which was more employed than any other, became reduced in length during the course of the experiments, the end being ground off on several occasions on account of the choking of the tube. This capillary is then described as C shortened. It did not seem requisite to give in every case the dimensions of the bulb and capillary tube, as all the experiments were conducted on the same plan, and the transpiration of water is in every case given as a standard of comparison. Direct experiments were also made, which proved that the transpiration-times were sensibly inversely proportional to the effective pressure applied to the liquid, as found by POISEUILLE; which indicates that the capillaries offered sufficient resistance to the passage of the liquid.

Sulphuric Acid.

TABLE II.—Transpiration of Sulphuric Acid, at 20°, by Capillary G.
(Transpiration-time of water, 109 seconds.)

Water added to 100 acid (SHO_4).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water=1.	
0	0	2360	21·6514	1·8456
2·5	2·43	2412	22·1284	1·8398
5	4·76	2451	22·4862	1·8346
10	9·09	2516	23·0825	1·8120
12·5	11·11	2548	23·3761	1·7976
15	13·04	2587	23·7340	1·7800
17·5	14·89	2591	23·7706	
18·36 ... 1 eq. HO	15·13	2466	22·6238	1·7590
20	16·66	2398	22·0000	1·7473
30	23·07	1523	13·9724	1·6700
36·73 ... 2 eqs. HO	26·86	1189	10·9090	1·6335
40	28·50	1056	9·6880	1·6146
50	33·33	810	7·4302	1·5600
60	37·50	626	5·7431	1·5118
70	41·17	535	4·9082	
80	44·44	450	4·1284	
100	50·00	382	3·5045	
120	54·54	332	3·0458	
140	58·33	290	2·6605	
160	61·53	260	2·3889	
180	64·28	241	2·2110	
200	66·66	227	2·0825	

The transpiration of sulphuric acid is very slow, being twenty-four times less rapid than that of water, as might be expected from the viscous quality of the acid fluid. It is surprising, however, that the first additions of water do not promote the transpiration, although they lessen in a sensible degree the viscosity of the liquid. The transpiration-time increases from 2360 to 2591 seconds, and then attains the maximum, when 17·5 parts of water have been added to 100 parts of oil of vitriol. The proportion of water named approaches closely to 1 equivalent (18·36 parts). Indeed it is quite possible that the acid mixture which exhibits the least transpirability might have contained a full equivalent of water, for a portion of aqueous vapour may have been absorbed from the air during the process of filling the bulb. That the crystallizable hydrate of sulphuric acid, SHO_4+HO, is the liquid of least transpirability is, I believe, the proper inference from these observations. With increasing proportions of water the transpiration-time rapidly diminishes, till the time is reduced to 227 seconds in a mixture of oil of vitriol with twice its weight of water.

A more minute examination than has been attempted would be required to show whether the existence of other definite hydrates of sulphuric acid may be indicated by a perceptible retardation in the time of transpiration.

Acetic Acid.

TABLE III.—Transpiration of Acetic Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid ($C_4H_4O_4$).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water =1.	
0·8	0·8	445·5	1·2801	
15 ... 1 eq. HO	13·04	890	2·5574	1·0735
20	16·66	921·5	2·6480	1·0742
25	20·00	931	2·6753	
27·5	21·56	933	2·6810	
30 ... 2 eqs. HO	23·07	941	2·7040	1·0752
32·5	24·52	934	2·6839	1·0746
35	25·92	928	2·6666	
40	28·50	912	2·6207	
45	31·04	895	2·5718	
50	33·33	882	2·5344	1·0720
60 ... 4 eqs. HO	37·50	852	2·4482	1·0700
90 ... 6 eqs. HO	47·36	769	2·2098	

The glacial acetic acid made use of in these experiments still retained 0·8 per cent. of water. Its transpiration-time was 445·5 seconds. With the addition of 1 equiv. of water the time rose to 890 seconds; and with 2 equivs. of water to 941 seconds, when it attained its maximum. This last is the characteristic hydrate of acetic acid, $C_4H_4O_4+2HO$. It is marked out with great precision in these transpiration experiments. The times rise very gradually on either side, and appear to culminate exactly at that point. It is also the compound of water and acetic acid of maximum density, as is well known. The transpiration-time of the hydrate referred to is so much as 2·7 times longer than that of pure water. With 6 equivalents of water acetic acid is still transpired 2·2 times more slowly than water.

Butyric Acid.

TABLE IV.—Transpiration of Butyric Acid, $C_8H_8O_4$, at 20°, by Capillary C shortened.

(Transpiration-time of water, 290 seconds.)

Water added to 100 acid ($C_8H_8O_4$).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water =1.	
0	0	454	1·565	·9740
10·22 ... 1 eq. HO	9·27	828	2·855	·9901
20·45 ... 2 eqs. HO	16·98	951	3·279	·9975
30·67 ... 3 eqs. HO	23·47	969	3·341	
38·69 ... 4·8 eqs. HO	27·85	863	2·975	

In the transpirability of its hydrates butyric acid presents a considerable analogy to acetic acid, as might be expected from the relation of these acids in composition. The time of the acid ($C_8H_8O_4$) is 1·565, referred to that of water as 1, and it rises to 2·855 by the addition of 1 equivalent of water. By a second equivalent of water the time is increased to 3·279. Here, however, the progression does not immediately turn, as with acetic acid, but the time rises to 3·341 with 3 equivalents of water. With 3·8 equivalents of water the time is 2·975, and has accordingly very sensibly receded, the maximum point being passed. It is conceivable that the relation to acetic acid is slightly modified in butyric acid by the interference of some other physical property, such as unctuosity, that is unequally developed in the two acids.

Valerianic Acid.

The hydration of this acid cannot be carried beyond 2 equivalents, but up to that point the transpiration is retarded by every addition of water, as in acetic and butyric acids. While the basic hydrate ($C_{10}H_{10}O_4$) is transpired in 2·155 times the water period, the time increases to 3·634 with 1 equivalent of water added, and to 3·839 with 2 equivalents.

TABLE V.—Transpiration of Valerianic Acid, at 20° C., by Capillary C shortened.
(Transpiration-time of water, 290 seconds.)

Water added to 100 acid ($C_{10}H_{10}O_4$).	Water per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0	0	625·2	2·155	·9350
8·82 ... 1 eq. HO	8·10	1054	3·634	·9484
17·64 ... 2 eqs. HO	15·84	1113·5	3·839	·9519

Formic Acid.

Formic acid appears to diverge considerably from the other members of the acetic acid series in certain physical and chemical characters. While the acetic hydrate is lighter than water, and is increased in density by the addition of water, the formic hydrate has a higher density than water, and has its density uniformly lowered by dilution, as will be seen in the Table which follows. The transpiration-time of formic acid is also highest in a concentrated state, and diminishes with dilution in the same regular manner as the density, showing no evidence of the acetic maximum at the point of 2 equivalents of water. Indeed, formic acid does not appear to affect that particular degree of hydration so characteristic of the acetic acid series. Hence it is, also, that we have no subformiate of lead corresponding with the subacetate of lead, and have occasion to remark a general absence of basic formiates. The physical properties of liquid formic acid are more suggestive of hydrochloric acid than they are of acetic acid.

The most concentrated formic acid that could be prepared still contained 3·6 per cent. of water. The transpiration-time of that liquid, it will be seen, is 1·718 referred to water as 1; and of the 2-hydrate 1·486. There is evidence of retardation between the points of 3 and 4 equivalents of water, but it is difficult to say with which of these two hydrates the retardation should be connected. More numerous and minute observations would be required to settle the point. We can only draw the negative conclusion from the Table, that the maximum retardation does not coincide with the 2-hydrate as in acetic acid.

Table VI.—Transpiration of Formic Acid, at 20°, by Capillary C shortened.
(Transpiration-time of water, 293 seconds.)

Water added to 100 acid ($C_2H_2O_4$).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water =1.	
3·73	3·6	503·5	1·718	1·2265
19·56 ... 1 eq.	16·35	484·5	1·653	1·2019
39·13 ... 2 eqs.	20·93	435·5	1·486	1·1765
58·69 ... 3 eqs.	36·98	411	1·402	1·1524
68·47 ... 3·5 eqs.	40·64	401·5	1·368	1·1466
78·26 ... 4 eqs.	43·90	402·5	1·372	1·1408
97·82 ... 5 eqs.	49·44	388·5	1·325	1·1275
117·35 ... 6 eqs.	53·99	376·5	1·284	1·1203
136·95 ... 7 eqs.	57·79	359	1·225	1·1062

Hydrochloric Acid.

The most concentrated form of this acid that was dealt with, acid of sp. gr. 1·1553, contained already upwards of 8 equivalents of water. Its transpiration-time was 1·7356, referred to the time of water as 1. With further dilution the time diminished, till at the proportion of 12 equivalents of water the time had fallen to 1·5287. About this point the rate of diminution is reduced, and the transpiration-time even becomes stationary for a short portion of the range of hydration. The retardation observed appears to coincide with the formation of a 12-hydrate of hydrochloric acid. The existence of such a compound is further supported by the fact that solutions of hydrochloric acid tend to the same composition by evaporation at the atmospheric temperature. The degree of hydration of most stability at high temperatures, and having the highest boiling-point, is known to be at or near the proportion of the 16-hydrate. The existence, however, of the latter hydrate, at the ordinary temperature, is not supported by the transpiration experiments now recorded, conducted as these were at a low temperature.

Table VII.—Transpiration of Hydrochloric Acid, at 20°, by Capillary C.
(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (H Cl).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water =1.	
221·8	69·23	604	1·7356	1·1553
250	71·42	569	1·6336	1·1411
280	73·67	536	1·5404	1·1303
290	74·36	532	1·5287	
295·89 ... 12 eqs. HO	74·74	532	1·5287	1·1246
300	75·00	520	1·4942	
310	75·60	516	1·4827	1·1202
380	79·20	486	1·3965	1·1021
394 ... 16 eqs. HO	79·97	479	1·3764	1·0992
410	80·39	469	1·3476	1·0961

Alcohol.

The fundamental discovery made by POISEUILLE of a point of maximum retardation in the transpiration of diluted alcohol is fully confirmed in the following series of observations. The transpiration-time rises from that of absolute alcohol, 1·1957 (water being 1), to 2·7872, when the alcohol is united with 6 equivalents of water, and then falls off again by further additions of water.

TABLE VIII.—Transpiration of Alcohol, at 20°, by Capillary D.
(Transpiration-time of water, 470 seconds.)

Water added to 100 Alcohol.	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0	0	562	1·1957	
1	0·99	578	1·2297	·7069
3	2·91	615	1·3085	·8030
5	4·76	650	1·3829	·8083
7	6·54	695	1·4787	
10	9·09	734	1·5617	
20	16·66	851	1·8106	·8396
30	23·07	950	2·0212	·8557
40	28·50	1029	2·1893	·8683
50	33·33	1093	2·3253	·8800
60	37·50	1152	2·4510	·8897
70	41·17	1213	2·5808	·8983
72·5	42·02	1230	2·6170	·9003
75	42·85	1231	2·6191	·9021
78·26 ... 4 eqs. HO	43·94	1239	2·6361	·9045
80	44·44	1238	2·6340	·9058
82·5	45·20	1242	2·6425	·9073
85	45·94	1244	2·6468	·9088
90	47·36	1256	2·6723	·9120
100	50·00	1268	2·6978	·9183
110	52·38	1282	2·7276	·9235
112·5	52·94	1287	2·7382	·9249
115	53·49	1298	2·7617	·9255
117·39 ... 6 eqs. HO	54·04	1310	2·7872	·9271
120	54·54	1307	2·7808	·9288
122	55·05	1300	2·7659	·9292
125	55·55	1297	2·7595	·9304
130	56·52	1297	2·7595	·9328
140	58·33	1295	2·7553	·9363
150	60·00	1280	2·7234	·9396
160	61·53	1255	2·6702	·9430
170	62·92	1250	2·6505	·9451
180	64·28	1246	2·6510	·9482
190	65·51	1240	2·6382	·9500
200	66·66	1235	2·6276	·9521
250	71·42	1165	2·4787	·9601
300	75·00	1094	2·3276	·9652
350	77·77	1026	2·1829	·9689
400	80·00	973	2·0702	·9716
450	81·80	934	1·9872	·9738
500	83·33	908	1·9319	·9759

It will be observed that after attaining its maximum the transpiration-time falls off in a very gradual manner, till another equivalent at least of water has been added. With still further dilution the shortening of the transpiration-time is considerably more rapid. The Table appears to indicate a slight retardation at the proportion of four equivalents of water; but this would require confirmation. It is remarkable that hydrated liquid compounds appear in general to show only one decided transpiration maximum, as with the 1-hydrate in sulphuric acid, the 2-hydrate in acetic acid, the 3-hydrate in nitric acid, the 6-hydrate in alcohol, and the 12-hydrate in hydrochloric acid.

A considerable number of experiments were made upon specimens of *methylic alcohol* prepared at different times, with some discrepancy in the results. Although always derived from crystallized methylic oxalic ether, the liquid varied sensibly in transpirability. As the cause of this variation has not yet been ascertained, I shall confine myself at present to one statement, namely, that a particular specimen of methylic alcohol gave 0·63 as the transpiration-time of the anhydrous substance (water being 1), and 1·8021 as the time of the 6-hydrate, $C_2 H_4 O_2 + 6HO$, and that for a considerable distance on either side of that point of hydration the transpiration was slightly less and nearly constant, as it is in vinic alcohol. It may be inferred, therefore, with some probability, that alcohols have a maximum of retardation at the same stage of dilution.

Three alcohols in a state of purity were transpired through the same capillary, with water for comparison, at 20°. The time of water was 297 seconds.

TABLE IX.—Transpiration of Alcohols, at 20°.

	Transpiration-time.		Specific gravity, at 15°.	Boiling-point.
	In seconds.	Water=1.		
Methylic alcohol	187·25	0·630	·7973	66° C.
Vinic alcohol..............	355·1	1·195	·7947	78·5
Amylic alcohol	1084	3·649	·8204	132

It will be remarked that the transpiration-time of an alcohol increases with the elevation of its temperature of ebullition. A similar observation applies to the transpiration of ethers.

TABLE X.—Transpiration of Ethers, at 20°, by Capillary C shortened.
(Transpiration-time of water, 290 seconds.)

	Transpiration-time.		Specific gravity, at 15°.	Boiling-point.
	In seconds.	Water=1.		
Formiate of ethyl	148·2	0·511	·9174	55°·5
Acetate of ethyl	160·5	0·553	·8853	74
Butyrate of ethyl	217·5	0·750	·8490	114
Valerianate of ethyl	237·5	0·827	·8750	133·5

The transpiration-times of the homologous acids, previously observed, appear also to follow in progression.

Transpiration of Acids, at 20°.

	Acid.	Acid +2HO.
Acetic acid	1·2801	2·740
Butyric acid	1·565	3·279
Valerianic acid	2·155	3·839

The increase of the transpiration-time of an alcohol, ether, and acid, as each rises in its series, may be connected with the increasing weight of their molecule.

Acetone.

The transpiration of this liquid is remarkably rapid. It is also greatly retarded by the addition of water. The time will be found to rise from 0·401, that of anhydrous acetone, to 1·604, the time of the 12-hydrate, taking the equivalent of acetone as $C_6H_6O_2$, or of the 6-hydrate with the equivalent C_3H_3O.

TABLE XI.—Transpiration of Acetone, at 20°, by Capillary C.
(Transpiration-time of water, 348 seconds.)

Water added to 100 acetone ($C_6H_6O_2$).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water=1.	
0	0	139·6	0·401	·7943
15·51 ... 1 eq.	13·42	212·5	0·610	·8384
31·03 ... 2 eqs.	23·68	283·5	0·814	·8604
46·55 ... 3 "	31·76	355·5	1·021	·8850
62·06 ... 4 "	38·29	457	1·313	·8990
77·58 ... 5 "	43·68	464	1·333	·9123
85·34 ... 5·5 "	46·04	469	1·347	·9173
93·10 ... 6 "	48·21	482	1·385	·9219
100	50·00	500	1·436	·9251
108·61 ... 7 "	52·06	515·5	1·479	·9300
124·13 ... 8 "	55·33	531·5	1·527	·9320
139·65 ... 9 "	57·85	537·7	1·543	·9413
155·16 ... 10 "	60·81	552·7	1·586	·9468
170·67 ... 11 "	63·05	555·5	1·594	·9504
186·18 ... 12 "	65·05	558·5	1·604	·9526
201·71 ... 13 "	66·85	556·5	1·599	·9563
217·24 ... 14 "	68·41	557	1·600	·9588
232·75 ... 15 "	69·94	553·5	1·590	·9608
248·27 ... 16 "	71·28	549	1·577	·9632
263·79 ... 17 "	72·23	547	1·571	·9649
279·31 ... 18 "	73·63	546	1·568	·9662
294·82 ... 19 "	74·67	539·5	1·550	·9676
372·24 ... 24 "	78·82	519	1·491	·9736

The transpiration-time of acetone attains a maximum at what is represented in the Table as the compound with 12 equivalents of water. The time is nearly stationary for some distance on either side of that point, the range from 10 to 15 equivalents of water being 1·586 to 1·590, with 1·604 as a maximum for the intermediate twelfth equivalent.

Glycerine.

This liquid is too viscid in a state of purity to be transpired by means of the bulb and capillaries employed in these experiments. The observations to be recorded were confined to diluted solutions of glycerine approaching in composition to the 18-hydrate, $C_8H_8O_6+18HO$. It was imagined that glycerine as a triatomic alcohol might affect combination with water in the proportion named.

TABLE XII.—Transpiration of Glycerine, at 20°, by Capillary C.

(Transpiration-time of water at the same temperature, 348 seconds.)

Water added to 100 Glycerine ($C_6H_8O_6$).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
170	62·96	1199	3·445	1·1010
176·07 ... 18 eqs.	63·77	1160	3·333	1·0980
180	64·28	1131·5	3·251	1·0960
190	65·51	1068·5	3·070	1·0934
192	65·75	1054	3·031	1·0927
195	66·10	1049	3·014	1·0914
197	66·32	1039	2·977	1·0912
200	66·66	1026	2·948	1·0905

The transpiration-time of 18-hydrate is 3·333, referred to water as 1. There is no indication of a maximum at that point, but the numbers descend according to their place in the Table without any interruption.

The idea having suggested itself that the viscous property of glycerine solutions might overpower or conceal the expected deviation, the transpiration was repeated at a higher temperature, when the solutions possess greater fluidity.

TABLE XIII.—Transpiration of Glycerine, at 60°, by Capillary C.

(Transpiration-time of water at the same temperature, 186 seconds.)

Water added to 100 Glycerine ($C_6H_8O_6$).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
170	62·96	435·5	2·341	1·1010
172·5	63·30	432	2·322	1·0999
175	63·63	428	2·301	1·0980
176·08 ... 18 eqs.	63·77	425	2·284	1·0976
177	63·96	422·5	2·271	1·0970
180	64·22	420	2·258	1·0960

Still no retardation appears at the point of 18 equivalents, but the time continues to shorten as the proportion of water is increased, according to a pretty uniform progression. The information respecting the constitution of glycerine which transpiration affords is therefore of a negative character.

The existence of a relation between the transpirability of liquids and their chemical composition appears to be established. It is a relation analogous in character to that subsisting between the boiling-point and composition, so well defined by M. KOPP. Perhaps the most interesting part of the present subject to develope would be the transpiration of homologous series of substances. Judging from the limited observations on the alcohols, ethers, and acids, the order of succession of individual substances in any series would be indicated by the degree of transpirability of these substances, as clearly as it is by their comparative volatility. In carrying out the inquiry, it would probably be found advantageous to operate at a fixed temperature, which is somewhat elevated. A large number of substances are liquid at 100°, of which the transpiration-time could be easily obtained.

In hydrated substances transpiration also affords a manifestation of definite combination at once striking and precise. I need only refer to the manner in which the "constitutional" hydrate of sulphuric acid SHO_4+HO, of acetic acid $C_4H_4O_4+2HO$, of nitric acid NHO_6+3HO, and of alcohol $C_4H_6O_2+6HO$ is each indicated by its maximum transpiration-time. The indication of the alcohol-hydrate is particularly distinct, although that hydrate must be a comparatively feeble compound. Indeed the extent to which transpiration is affected by the annexation of constitutional water appears to be by no means in proportion to the intensity of combination.

The increased resistance to transpiration observed in these definite hydrates may be connected with their larger molecules. But another speculative view of the retardation can be suggested, in which the phenomenon is referred to a physical agency. When one of these definite hydrates, say the 6-hydrate of alcohol, is being forced through the capillary, it may be imagined that a small portion of the hydrated compound is molecularily decomposed by the friction. A certain portion of the impelling force would thereby be lost, being converted into the latent heat which alcohol and water require to assume when separated from each other, and the transpiration be consequently retarded; for as alcohol and water evolve heat on combining, so they must absorb heat when their union is dissolved by any cause. But the change of temperature representing the lost force appears to be too small to be rendered sensible to observation. It would be capable of raising the temperature of the transpired liquid not more than about one forty-third part of a degree, according to an accurate estimate for which I am indebted to Professor STOKES. In consequence of this circumstance the physical hypothesis now suggested has neither been verified nor disproved.

To this paper are appended two series of observations made on transpiration at different temperatures, the first series being the transpiration of water, and the second that of absolute alcohol. Each series of experiments is repeated with two capillary tubes, one having nearly double the resistance of the other. The numbers from the two capillaries exhibit a fair amount of agreement. The times given are those actually observed, no correction being made for the small variation of the capillary in diameter at different temperatures.

The dimensions of Capillary D were as follows:—Capacity of bulb, 4·135 cub. cent.; length of capillary tube, 37·5 millims.; diameter of bore, 0·10325 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 470 seconds.

The dimensions of Capillary E were as follows:—Capacity of bulb, 3·725 cub. cent.; length of capillary, 53 millims.; diameter of bore, 0·0858 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 913 seconds.

TABLE XIV.—Transpiration of Water at different Temperatures.

Temperature.	By capillary tube D.					By capillary tube E.				
	Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.		Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.	
		Time.	Velocity.	Time.	Velocity.		Time.	Velocity.	Time.	Velocity.
0°	840	1·7872	0·5593	1·	1·	1629	1·7872	0·5604	1·	1·
1	792	1·6851	0·5934	0·9428	1·0606	1568	1·7174	0·5829	0·9625	1·0389
2	770·5	1·6391	0·6099	0·9172	1·	1514	1·6582	0·6050	0·9294	1·
3	749	1·5936	0·6275	0·8917	1·1216	1461	1·6002	0·6249	0·8975	1·1449
4	727	1·5468	0·6465	0·8654	1·					
5	709	1·5085	0·6629	0·8440	1·1857	1382	1·5136	0·6606	0·8483	1·1787
7	669	1·4234	0·7025	0·7964	1·2556	1289	1·4118	0·7083	0·7912	1·2638
10	618	1·3148	0·7605	0·7357	1·3592	1188	1·3012	0·7685	0·7293	1·3717
14	548	1·1659	0·8576	0·6423	1·5328					
15	533	1·1340	0·8818	0·6345	1·5759	1037	1·1358	0·8804	0·6366	1·5709
16	521	1·1085	0·9021	0·6202	1·6122					
20	470	1·	1·	0·5595	1·7872	913	1·	1·	0·5604	1·7842
25	414	0·8808	1·1352	0·4928	2·0189	823	0·9014	1·0904	0·5052	1·9793
30	375·5	0·7989	1·2516	0·4470	2·2371	743	0·8138	1·2288	0·4501	2·1924
35	338	0·7191	1·3905	0·4023	2·4852	670	0·7338	1·3626	0·4113	2·4313
40	309·5	0·6508	1·5185	0·3684	2·7108	602	0·6593	1·5166	0·3695	2·7059
45	284·5	0·6053	1·6520	0·3386	2·9525	553	0·6056	1·6509	0·3394	2·9459
50	261	0·5553	1·8007	0·3107	3·2184	505	0·5531	1·8079	0·3100	3·2257
55	243	0·5170	1·9341	0·2892	3·4979	475	0·5202	1·9221	0·2916	3·4294
60	228	0·4851	2·0614	0·2714	3·6842	438	0·4797	2·0844	0·2689	3·7191
65	214	0·4553	2·1967	0·2547	3·9252	400	0·4381	2·2825	0·2455	4·0725
70	200	0·4155	2·3500	0·2380	4·2000	378	0·4140	2·4153	0·2321	4·3122

TABLE XV.—Transpiration of Alcohol at different Temperatures.

Temperature.	By capillary tube D.					By capillary tube E.				
	Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.		Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.	
		Time.	Velocity.	Time.	Velocity.		Time.	Velocity.	Time.	Velocity.
0 °C.	860	1·8297	0·5465	1·0238	0·9767	1642	1·7984	0·5560	1·0079	0·9920
1	840	1·7893	0·5588	1·0012	0·9988	1601	1·7535	0·5702	0·9828	1·0174
3	807	1·7170	0·5824	0·9607	1·0409	1537	1·6834	0·5940	0·9435	1·0598
5	772	1·6425	0·6089	0·9190	1·0880	1473	1·6133	0·6198	0·9042	1·1059
7	738	1·5702	0·6368	0·8785	1·1382	1410	1·5443	0·6475	0·8656	1·1553
10	700	1·4893	0·6714	0·8333	1·2000	1350	1·4786	0·6755	0·8226	1·2066
15	624	1·3276	0·7532	0·7428	1·3461	1213	1·3285	0·7526	0·7446	1·3429
20	562	1·1957	0·8362	0·6690	1·4946	1092	1·1960	0·8360	0·6703	1·4917
25	520	1·1063	0·9038	0·6190	1·6154	1001	1·0963	0·9120	0·6145	1·6273
30	476	1·0127	0·9873	0·5566	1·7646	915	1·0022	0·9978	0·5617	1·7803
35	428	0·9106	1·0981	0·5095	1·9626	843	0·9233	1·0830	0·5175	1·9323
40	391	0·8319	1·2020	0·4654	2·1483	772	0·8455	1·1826	0·4739	2·1101
45	360	0·7659	1·3055	0·4285	2·3333	707	0·7743	1·2913	0·4340	2·3041
50	331·5	0·7053	1·4177	0·3946	2·5339	645	0·7064	1·4155	0·3959	2·5100
55	307	0·6531	1·5309	0·3654	2·7301	592	0·6484	1·5422	0·3634	2·7517
60	285	0·6063	1·6491	0·3392	2·9473	551	0·6035	1·6569	0·3382	2·9564
65	262	0·5574	1·8005	0·3119	3·2061	510	0·5585	1·7901	0·3130	3·1941
70	241	0·5127	1·9502	0·2869	3·4854	468	0·5125	1·9465	0·2873	3·4807