XIV. BARGER'S MICROSCOPICAL METHOD OF DETERMINING MOLECULAR WEIGHTS.

PART I. THE PRINCIPLE OF THE METHOD WITH REFERENCE TO THE MOLECULAR AND IONIC ATTRACTION OF SOLUTE FOR SOLVENT.

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(Received February 24th, 1920.)

A VERY reliable and convenient method has been described by Barger [1904] for determining molecular weights, which is explained by the author to be based upon the vapour pressure.

Its usefulness for studying the degree of association of acids, phenols, etc., when dissolved in mixtures of an associative and a non-associative liquid, has been proved by his interesting work which was published in the following year.

The technique of this method is quite simple. Series of drops, taken from two solutions, the one the standard, the other a given solution, of which the molecular weight of the solute is to be determined, are alternately introduced into a capillary tube, and the change in the length of the drops is studied by means of a micrometer. If one series of drops is observed to have increased while those alternating with them have decreased, it is to be assumed that the solution from which the former series of drops was taken has a higher molecular concentration than the latter.

The given solution is thus compared with a series of standard solutions of known molecular concentrations and in this way two limits are reached for the unknown molecular concentration.

The mechanism of this method is explained by Barger in the following way: "Each drop is placed between two others of a different solution and can evaporate on either side into a small air chamber. This closed air chamber is soon saturated with vapour, which can condense freely on the drops. If the vapour pressures of the two solutions are equal, the evaporation will equal the condensation, and there will be no change in the drops. If, on the other hand, the vapour pressures are unequal, there will be a gradient of the vapour pressure in the air spaces; some drops will therefore be in contact with an atmosphere, the vapour pressure of which is greater than their own.

Condensation will take place on these drops and they will increase. The others, alternating with them, have a vapour pressure greater than that of the adjoining air spaces; these drops will evaporate and thus decrease. Hence there is distillation from drops of the one series to those of the other series, although all are at the same temperature."

In the course of an investigation of caseinogen solutions by this method, I have observed some facts which made me think it impossible to ascribe the mechanism of this method solely to vapour pressure.

I was determining the molecular and ionic concentration of alkali caseinogenate solutions, employing urea solutions as the standard. But it was feared that urea might combine with the alkali contained in the caseinogenate solutions. As Barger states in his paper, substances which may combine with the solute of the solutions employed are not to be used as standards because a certain amount of mixing of the two solutions is inevitable. All the drops of both series are successively taken in from one end of the capillary tube, so that the wall of the tube is wetted by each drop alternately. Therefore, not only the drops of one series are contaminated with the other solution when they are taken in, but also it cannot be denied that the drops remain in contact with each other by means of a thin layer of a mixture of the two solutions. Hence it becomes necessary that the standard substance should not combine chemically with the substance of unknown molecular weight.

Under these circumstances, I tried to modify the method in such a way that this limitation in the choice of the standard substance might be removed.

At first sight this appeared to be very easy because I thought a satisfactory result would always be obtained if the two solutions were brought into a closed air space avoiding contact with each other.

But this was not the case. The volume change of solutions thus confined in an air-tight chamber was found to proceed extraordinarily slowly, if they were not allowed to touch each other, even when the two solutions were very close together. Such fairly regular and rapid change in volume of the solutions, as is seen in Barger's method, was very difficult to obtain.

The protocol of the experiments described in the following section illustrates this fact.

Experiment I. In the capillary tubes which are generally employed in Barger's method two small drops of solutions of different molecular concentrations were introduced from either end of the tube, so that the wall of the tube between the drops was left partly unwetted by the solutions. The lengths of the tubes were all 8 cm. The first drop was introduced in the usual way and allowed to slide down to the middle of the tube and then the other drop was introduced from the other end and allowed to slip down for a distance of 2 cm., the first drop, accordingly, going back to a point 2 cm. away from the other end. Each drop therefore stood 2 cm. away from its respective end and 4 cm. away from the other; 2 cm. of the wall of the tube between the drops remained dry, while the other 2 cm. were wetted by the first drop.

The ends of the tubes were then carefully sealed by heating. The tubes were then placed under water in Petri dishes, and the change of the drops at room temperature, 12°–16.5°, was studied every 24 hours, after the initial length of the drops had been measured immediately after the preparation of the tubes.

The results are given in Table I, in tenths of scale divisions, as explained below after Table III.

Table I.

No. of tube	Diameter of tube	Change in length of drop No. 1 (0.5 <i>M</i> urea solution)							
		Initial length	1st 24 h.	2nd 24 h.	3rd 24 h.	4th 24 h.	5th 24 h.	6th 24 h.	7th 24 h.
1	480	520	-10	-10	-5	-3	—	—	—
2	443	530	-12	-12	-3	-2	—	—	—
3	450	420	-6	-6	-10	-8	—	—	—
4	400	413	-8	-7	-5	-5	—	—	—
5	510	212	-13	-5	-4	-2	0	0	+2
6	467	242	-8	-3	-3	+2	+5	0	+3
7	492	356	-11	-13	-0	-0	-2	+1	-1

No. of tube	Diameter of tube	Change in length of drop No. 2 (0.1 <i>M</i> urea solution)							
		Initial length	1st 24 h.	2nd 24 h.	3rd 24 h.	4th 24 h.	5th 24 h.	6th 24 h.	7th 24 h.
1	480	462	-46	-42	-40	-21	—	—	—
2	443	236	-41	-42	-15	-40	—	—	—
3	450	436	-48	-30	-35	-15	—	—	—
4	400	630	-42	-30	-18	-16	—	—	—
5	510	322	-47	-41	-24	-19	-15	-8	-17
6	467	760	-30	-42	-25	-17	-6	-15	-9
7	492	449	-43	-27	-5	-16	-18	-7	-5

It will be easily realized how quickly and regularly the change of drops takes place in Barger's method, if the above protocol is compared with the change of drops observed under normal conditions, as is shown in Table II.

Experiment II. 0.5 *M* solution of urea was compared with 0.1 *M* solution. In Table II the drops indicated by odd numbers are those of 0.5 *M* solution, and the even numbers denote the drops of 0.1 *M* solution. The lengths of the air spaces between the drops were also measured in order to make the relation of each drop clear (they are placed in brackets).

Table II.

No. of tube	Drops					Diameter of tube
	1	2	3	4	5	
1 (860)	585 +13 (925)	550 (1150) -12	528 (840) +8	600 (870) -15	601 (1200) +9	460
2 (950)	683 +14 (1080)	540 (847) -15	522 (705) +8	680 (824) -14	521 (915) +14	445
3 (1045)	487 +10 (1210)	479 (920) -17	545 (965) +17	569 (1030) -12	500 (995) +11	515

The initial measurement was made immediately after the preparation of the tubes, and the second determination was made 2.5 hours afterwards at room temperature, 15°.

As shown in Table II, the change in the lengths of the drops is quite decisive, the drops of the stronger solution increasing regularly and the drops of the weaker solution decreasing, only 2.5 hours after the preparation of the tubes, whereas such a change does not occur even after 100 hours at the same temperature and with the same solutions if the drops are 4 cm. apart and 2 cm. of the wall between the drops is left dry, as described in Exp. I, Table I. The difference between the drop-changes in these two cases seems too great to be attributed solely to the greater distance between the drops in Exp. I. That vapour pressure plays only a subsidiary part results also from experiments which were made with solutions of which an accurately known volume (about 0.4 cc.) was delivered on to weighed dry filter papers (3 × 12 cm.) placed parallel and face to face 6–7 mm. apart in stoppered glass cylinders at 37°. After 24 hours the cylinder was weighed before and after the removal of each paper separately, thus giving the weight of the papers by difference. Both papers invariably lost weight (0.06–0.15 g.) and no sort of regularity could be discerned unless the papers were allowed to touch after the solutions had been uniformly distributed in them. In that case it was possible to distinguish between 0.1 and 0.166, and between 0.1 and 0.05 molar concentrations, by the differences in the loss of weight.

These experiments with tubes and filter papers compelled me to doubt the importance of the vapour pressure in causing the change of drop-length in Barger's method.

The next experiment seems to prove definitely the existence of a factor other than the vapour pressure, the action of which appears to depend on the fact that the two solutions are in contact.

Experiment III. 0.5 *M* and 0.25 *M* aqueous solutions of urea, boric acid and cane sugar were prepared and the drop-change according to Barger's method was investigated in the two series.

Now, if the change of volume of the drops is produced solely by the difference in vapour pressures of neighbouring drops, this change must stop when the concentrations have all become equal, owing to the dilution of the drops of the stronger solution, and the concentration of the drops of the weaker solution by evaporation. The decrease in volume of drops taken from 0.25 *M* solutions must cease before their original length is halved, because their molecular concentration must be 0.5 at this point, if the decrease has taken place only by evaporation of the solvent.

If the drops of 0.25 *M* solution had ever been shown to have become just half of their initial volume, it would mean that distillation had proceeded from the stronger solution to the weaker, for the concentration of the 0.25 *M* drops would then be 0.5 *M*, while that of the drops of 0.5 *M* solution would be correspondingly weaker than 0.5 *M*.

This remarkable result has, indeed, been observed. The decrease in length of drops taken from 0.25 *M* solution actually proceeded until they were less than one-third of their original length, as shown in Table III (a), (b), (c).

It is impossible to explain this experimental observation without assuming that the drop-change occurred because of a transference, not only of vapour, but also of liquid from the weaker to the stronger solution, that is, the stronger solution attracted the solvent of the weaker solution through the film furnished by the liquid membrane which extended between the two drops. As the liquid membrane, differing from the semipermeable membrane which is generally employed in osmotic pressure experiments, is perfectly permeable for both solute and solvent, so the dissolved solute molecules have accompanied the solvent molecules to the stronger solution and consequently the 0.25 *M* drops were not correspondingly concentrated when diminution of their volume occurred.

Similarly, the dilution of the stronger solutions did not go parallel with the increase of their volume, which would be expected if the increase of the drops were caused by condensation of vapour only.

This seems to be the most probable explanation for the further increase of the volume beyond the point at which it would stop if the change depended solely on vapour pressure.

Table III (a)

30 hours at 35° C.										Diameter of tube
	1 (0.25 <i>M</i>)	2 (0.5 <i>M</i>)	3 (0.25 <i>M</i>)	4 (0.5 <i>M</i>)	5 (0.25 <i>M</i>)					
Urea	(850) 270 135	(750) 532 640	(1070) 264 140	(960) 600 740	(910) 254 110	(750)				455
"	(850) 304 140	(845) 684 890	(1020) 270 125	(860) 642 765	(1200) 230 101	(710)				515
Boric acid	(1000) 145 35	(850) 635 725	(990) 172 55	(888) 650 780	(940) 210 70	(775)				465

(b)

30 hours at 35° C.										Diameter of tube
	1 (urea)	2 (sugar)	3 (urea)	4 (sugar)	5 (urea)					
Sugar, 0.5 <i>M</i>	(890) 193	(680) 521	(810) 274	(800) 630	(850) 290	(1000)				480
Urea, 0.25 <i>M</i>	35	670	95	800	110					
"	(890) 430 280	(1110) 360 510	(900) 395 240	(1030) 380 520	(1150) 460 310	(1300)				525
"	(1150) 304 151	(1000) 740 890	(860) 325 170	(1090) 695 850	(980) 220 55	(1060)				510

(c)

5 days at 13–16° C.										Diameter of tube
	1 (0.25 <i>M</i>)	2 (0.5 <i>M</i>)	3 (0.25 <i>M</i>)	4 (0.5 <i>M</i>)	5 (0.25 <i>M</i>)					
Urea	(895) 383 173	(945) 781 1004	(1005) 423 210	(1100) 867 1060	(975) 447 235	(1000)				445
"	(1030) 445 218	(965) 817 1030	(749) 390 177	(1010) 720 930	(940) 464 261	(920)				430
Boric acid	(910) 350 169	(744) 606 806	(780) 266 94	(772) 640 865	(916) 340 126	(850)				525

The measurement of the drop-length was made with the ocular micrometer 0.1 mm. No. 2 and Leitz objective No. 2.

One scale division of this micrometer corresponded to $\frac{1}{37}$ mm. when tested by means of a Carl Zeiss objective micrometer, 0.01 mm. The readings were made and are recorded throughout this paper in tenths of scale divisions. As the length of the intervals between the drops varied from 750 to 1400 tenths of a scale division, so the actual lengths of the intervals in the experiments were 2–4 mm., that is, a little greater than those indicated by Barger.

The fact that the 0.25 *M* drops decrease until they are less than one-third of their original length shows how small is the contribution of vapour pressure to the change of drops compared with the other factor.

In the following experiments the velocity of evaporation, which takes place from the surfaces of drops confined in glass tubes, was investigated in the case of aqueous solutions of various concentrations, by measuring the decrease in length after standing for some time at constant temperature.

The object of these experiments was to gain information as to the relative parts played by the vapour pressure and the second factor in changing the length of the drops in Barger's method.

Experiment IV. The leading idea of this experiment was that, if the vapour pressure is solely responsible for the change of drop-volume, then the difference between the velocity of evaporation of the weaker solution and that of the stronger solution must be equal to the magnitude of the volume-change in drops according to Barger's method, but if, on the other hand, the difference of these two velocities is not equal to the magnitude of the change, then the ratio of these two must represent the relative contribution of the vapour pressure and the other factor in bringing about the change.

The velocity of evaporation from the surface of the drops was found by measuring the decrease in their length when singly confined in capillary tubes.

The results thus obtained are presented in Table IV (a), (b), (c), (d).

Explanation of Table IV (a), (b). One small drop of distilled water was introduced into a capillary tube, both ends were carefully sealed and it was mounted on a glass slide, put in a Petri dish, and the decrease in length of the drop was observed at a constant temperature of 35°.

It was found that the drop thus confined in the capillary tube decreases in length fairly regularly with lapse of time. The length of the water drops decreased 80–96 tenths of a scale division during the first 24 hours. This appeared to be approximately the maximal amount which can evaporate from the surface of drops at this temperature and during this period, since increasing the length of the capillary tube did not result in a more rapid decrease of the drop-length. In an 8 cm. capillary tube, the amount of evaporation was not appreciably affected by the presence of another water drop near the other end of the tube.

This fact shows that the humidity of the air produced by evaporation during this period is not sufficiently great to influence appreciably the velocity

of evaporation. This conclusion is supported furthermore by the fact that the decrease in volume proceeds with almost the same speed during the next 24 hours.

In this experiment the approximate diameter of the capillary tube was measured, because it was feared that the surface dimension of the drops might not be exactly directly proportional to the diameter; in other words, the evaporating surface of a drop in a narrow tube might be relatively greater than that of a similar drop in a wider tube. But this apprehension proved to be unfounded. The amount of decrease was not influenced to any great extent by the difference of diameter within the variation of diameter of the tubes which we employed.

Table IV (a)

Single water drops in capillary tubes of varying length at 35° C.

No. of tube	Length of tube	Diameter of tube	Initial length of drops	Change in the 1st 2 hours	Change in the 1st 24 hours	Change in the 2nd 24 hours
1	6 cm.	450	726	- 4	-91	-85
2	8	460	962	- 8	-87	-90
3	10	455	453	- 6	-83	-88
4	12	400	775	- 5	-92	-94
5	14	430	680	-15	-98	-93

(b)

Two water drops in one tube (8 cm. long) at 35° C.

No. of tube	Diameter of tube	Drop No. I				Drop No. II			
		Initial length	1st 24 hours	2nd 24 hours	3rd 24 hours	Initial length	1st 24 hours	2nd 24 hours	3rd 24 hours
1	480	370	-86	-86	-79	466	-82	-80	-74
2	420	642	-85	-91	-69	440	-89	-81	-82
3	475	469	-86	-82	-67	303	-78	-76	-60
4	510	332	-84	-77	-74	496	-91	-85	-60
5	455	518	-87	-80	-71	421	-83	-83	-75

Explanation of Table IV (c), (d). When a substance was dissolved in the water, the velocity of evaporation expressed in terms of the diminution in length of the drops decreased with the concentration of the solution, as shown in Table IV (c), (d).

The amount of evaporation from drops of 0.5 *M* urea solution at a constant temperature of 35° in the first 24 hours varied from 28–39 tenths of a scale division, the mean decrease in length being 32.

Table IV (c)

Single drop and two drops of urea solution (0.5*M*) in one tube at 35° C.

No. of tube	Diameter of tube	Drop No. I				Drop No. II			
		Initial length	1st 24 hours	2nd 24 hours	3rd 24 hours	Initial length	1st 24 hours	2nd 24 hours	3rd 24 hours
1	480	469	-32	-12	- 8	—	—	—	—
2	410	332	-38	-23	- 3	—	—	—	—
3	505	308	-39	-21	-18	—	—	—	—
4	445	242	-31	-21	- 4	533	-39	-28	- 4
5	492	440	-34	-16	+ 2	442	-28	-18	-14
6	465	428	-30	-22	-11	415	-29	-24	- 8
7	460	302	-29	-14	- 6	320	-34	-16	- 2

The amount of evaporation from 0.25 *M* drops was found to be 53 tenths of a scale division as is shown in the Table IV (*d*).

Table IV (*d*)

Two drops of urea solution (0.25*M*) in one tube at 35° C.

No. of tube	Diameter of tube	Drop No. I				Drop No. II			
		Initial length	1st 24 hours	2nd 24 hours	3rd 24 hours	Initial length	1st 24 hours	2nd 24 hours	3rd 24 hours
1	420	244	-55	-36	-23	267	-44	-50	-32
2	440	501	-56	-35	-21	486	-52	-37	-20
3	510	320	-55	-37	-19	352	-57	-37	-11
4	435	382	-51	-42	-21	340	-54	-34	-26

Now if the change (increase and decrease) of volume of two drops in Barger's method is solely due to a difference of their vapour pressures, such volume-change should be equal to the difference between their decreases, when they are investigated separately as in Table IV (*a*)-(*d*), at the same temperature and for the same length of time.

The magnitude of change would, therefore, be expected to be about $87.4 - 32.0 = 55.4$ when 0.5 *M* urea solution is compared with distilled water.

In the same way, the drops would change their length 34.4 ($87.4 - 53.0$) when 0.25 *M* urea solution is compared with water, and 21.0 tenths of a scale division when 0.5 *M* solution is compared with 0.25 *M* solution.

But the change of drops actually observed at 35° for 24 hours was far greater than these calculated values (Table IV (*e*), (*f*), (*g*)).

The amount of change of the drops was 249, 148.5, 128.8 (mean values) respectively in the cases of 0.5 *M* : water; 0.25 *M* : water; and 0.5 *M* : 0.25 *M* (Table IV (*e*), (*f*), (*g*)).

The amount of change in the drops when compared at the same temperature for the same length of time was thus found to be about 5-6 times greater than the value calculated from the velocity of evaporation of each solution. It must be assumed therefore that the proportion of change due to the vapour pressure is only $\frac{1}{5}$ - $\frac{1}{6}$ of the entire change.

This ratio was also obtained in the case of boric acid solutions; when, however, lactose solution was investigated in this way, the ratio was a little smaller. The mean amount of evaporation from a single drop was respectively 0.5 *M* = 30, 0.25 *M* = 50, 0.1 *M* = 70.2, while the mean change of drops according to Barger's method was respectively

0.5 <i>M</i> : water	...	...	175
0.25 <i>M</i> : water	...	...	90
0.1 <i>M</i> : water	...	...	68
0.5 <i>M</i> : 0.25 <i>M</i>	...	...	68
0.5 <i>M</i> : 0.1 <i>M</i>	...	...	112
0.25 <i>M</i> : 0.1 <i>M</i>	...	...	53

Table IV (e)

The amount of volume change of drops in Barger's method, at 35° C., in the first 24 hours, 0.5 *M* urea compared with water.

No. of tube	Diameter of tube	1 (urea)	2 (water)	3 (urea)	4 (water)	5 (urea)
1	470	(1040)	635 + 246 (1100)	593 + 207 (1200)	676 - 231 (1210)	781 + 260 (1100)
2	415	(1070)	614 + 271 (1120)	586 - 201 (1180)	707 + 213 (1150)	680 + 270 (1280)
3	575	(980)	620 + 265 (1085)	640 - 235 (1060)	914 + 238 (990)	683 + 220 (1300)

The mean amount of volume change = 249 tenths of a scale division.

(f)

The amount of volume change of drops in Barger's method, at 35° C., in the first 24 hours, 0.25 *M* urea compared with water.

No. of tube	Diameter of tube	1 (urea)	2 (water)	3 (urea)	4 (water)	5 (urea)
1	470	(1510)	484 + 136 (1080)	599 - 129 (1070)	425 + 160 (830)	520 - 150 (1330)
2	510	(1315)	450 + 160 (940)	462 - 147 (1400)	365 + 130 (1250)	520 - 133 (1150)
3	440	(1225)	465 + 148 (985)	437 - 153 (1210)	442 + 138 (1345)	415 - 129 (980)

The mean amount of volume change = 148.5 tenths of a scale division.

(g)

The amount of volume change of drops in Barger's method, at 35° C., in the first 24 hours, 0.5 *M* compared with 0.25 *M* urea.

No. of tube	Diameter of tube	1 (0.5 <i>M</i>)	2 (0.25 <i>M</i>)	3 (0.5 <i>M</i>)	4 (0.25 <i>M</i>)	5 (0.5 <i>M</i>)
1	490	(860)	585 + 132 (925)	550 - 95 (1150)	520 + 114 (840)	471 - 124 (870)
2	425	(950)	683 + 121 (1080)	540 - 102 (845)	522 + 140 (705)	525 - 150 (624)
3	415	(980)	593 + 128 (985)	564 - 115 (725)	492 + 127 (965)	530 - 141 (910)

The mean amount of volume change = 128.8 tenths of a scale division.

(The numbers in brackets denote the lengths of the air spaces between the drops.)

The ratio between the calculated value and the actual amount for lactose solutions was respectively

0.5 <i>M</i> : water	...	...	3.0 : 1
0.25 <i>M</i> : water	...	...	2.4 : 1
0.1 <i>M</i> : water	...	...	4.0 : 1
0.5 <i>M</i> : 0.25 <i>M</i>	...	...	3.5 : 1
0.5 <i>M</i> : 0.1 <i>M</i>	...	...	2.8 : 1
0.25 <i>M</i> : 0.1 <i>M</i>	...	...	2.6 : 1

This small ratio probably does not indicate a greater part played by the vapour pressure here than in the case of urea or boric acid solutions, because

the evaporation of the single drops also takes place with a smaller speed than in the case of these latter solutions.

The probable explanation for this smaller ratio in the former case is that the molecules of sugar have a greater weight than those of urea and boric acid, hence the speed with which the former move in the solution is smaller than that of the latter. Now, in the case of the single drops, the surface of the drops becomes concentrated when evaporation proceeds, and this is also the case with the drops of weaker solutions in Barger's method, while the surface of the drops of stronger solutions becomes diluted by the entering of solvent.

It will take some time before these concentrated or diluted surface layers of the drops mix completely with the interior portions, causing the whole drop to become homogeneous. The slower the molecule moves the more time this diffusion will take, and thus the surface layer of the drops containing heavier molecules will remain longer in a concentrated or diluted condition than the surface of drops with lighter molecules.

This will result in slower evaporation of a solution with large molecules (this does not necessarily mean that the vapour pressure of such a solution is smaller). The smaller amount of evaporation, obtained in the single drop experiment, must have been due to this process. On the other hand, the volume-change of drops in Barger's method will be lessened by the slow mixing of the surface layer with the interior.

Thus the calculated amount and that actually observed are both influenced by the slowness of the movement of the molecules, and their ratio is affected doubly by this cause.

These ratios did not change when the same experiment was performed at 0°, although the amount of evaporation as well as the amount of the drop-change in Barger's method was reduced to $\frac{1}{4}$ of the value measured at 35°. It is of course evident that these ratios will change according to the length of the intervals between the drops. The part played by the streaming of solvent through the contact film of the drops will become smaller with the increase of the distance between them, so that the change of drops will be produced finally only by the difference of vapour pressure when some limit of distance has been exceeded. But under ordinary conditions, as directed by Barger (2-3 mm.), the amount of change ascribable to vapour pressure seems to be very small, and his method becomes quite unpracticable if the distance between the drops is so great that the drop-change is produced solely by the difference of vapour pressure.

The next question to be solved is what is the other factor which causes the volume-change of drops in this method. This cannot be other than the molecular and ionic attraction of solute for solvent, namely the force which is known also to give rise to the phenomenon of osmotic pressure. In this connection it seems to me that the "bombardment" theory of osmotic pressure, as represented in the text-books of Nernst, Lewis, Hedin, etc., is

less acceptable than van't Hoff's conception, particularly as explained more precisely by Mathews [1916].

"Osmosis" should be explained as a phenomenon of the wandering of the solvent molecules from a point where a weaker attractive power of solute molecules exists towards a point where a stronger attractive power is exerted. It does not matter whether there is a semipermeable membrane or not.

The force which produces the change of drops in Barger's method should thus be considered as the molecular-ionic attraction of solute for solvent.

Moreover, the change of the drops themselves seems to be due both to osmosis and to distillation, which are both caused by the same internal energy of solution, namely, the molecular-ionic attraction.

SUMMARY.

The principle upon which Barger's microscopical method of determining molecular weights is based has been studied, and it has been proved that the force which effects the volume-change of the drops is not simply the vapour pressure, but also the osmosis through the thin film of liquid between the drops. This latter factor plays the greater part in producing the change.

If the length of the intervals between the drops is 2-3 mm., $\frac{5}{8}$ to $\frac{7}{8}$ of the volume-change of the drops is attributable to osmosis.

Further, as osmosis as well as the lowering of vapour pressure are equally the results of one and the same internal energy of solution, that is, the molecular and ionic attraction of solute for solvent, which is of the same magnitude for all kinds of molecules and ions in the same solvent at the same temperature, it is possible to measure molecular weights or the degree of association or dissociation by investigating the volume-change of drops which are brought in contact with drops of standard solutions of known molecular concentrations.

In conclusion I wish to express my heartiest thanks to Dr C. J. Martin, the Director of the Lister Institute, who has kindly supplied me with material and apparatus. Prof. G. Barger, who has read this paper in manuscript, informs me that he is in general agreement with my conclusions. He has frequently observed the effect of Exp. III, when using organic solvents. Like myself in my experiments with filter papers he has entirely failed in repeated attempts to bring about a regular isothermic distillation in a closed space, when there was no film of liquid between two solutions differing only slightly in vapour pressure.

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