

## *A Thermal Method of Measuring the Vapour Pressure of an Aqueous Solution.*

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(Received January 16, 1930.)

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The method described below of measuring the difference of vapour pressure between any two aqueous solutions, or between a solution and the solvent, arose from experiments on isolated surviving muscles, in which it was noticed that stimulation in nitrogen led to a large increase in the rate of resting heat-production. This increment in heat rate was traced finally to condensation of moisture on the muscle, due to the lowering of vapour pressure caused in the muscle by the accumulation of the products of activity. These experiments are described elsewhere.\* The unexpected sensitivity of the apparatus to a change of vapour pressure led to its trial with solutions of various concentrations held by strips of filter paper; the results were so promising that a special instrument was designed and constructed, which alone is referred to in the following pages.

The method has various advantages: (a) it is direct† and fairly exact, *e.g.*, the difference of vapour pressure between water and a not too dilute aqueous solution can be measured at any required temperature, within 1 to 2 per cent.; (b) it is fairly rapid: a reading is obtained in 30 to 45 minutes and four or five measurements can be made at the same time, if desired, by a single observer; (c) it has a wide range, *e.g.*, one can measure, on the one hand, the difference of vapour pressure between 0.1 M. NaCl and 0.2 M. cane sugar, or, on the other, between 5 M. NaCl (5 g. molecules NaCl to 1000 g. H<sub>2</sub>O) and water, the latter difference being of the order of 500 times the former; (d) very small quantities of the solutions are required, enough namely to moisten 1 to 2 sq. cm. of filter paper, say 0.2 cc.

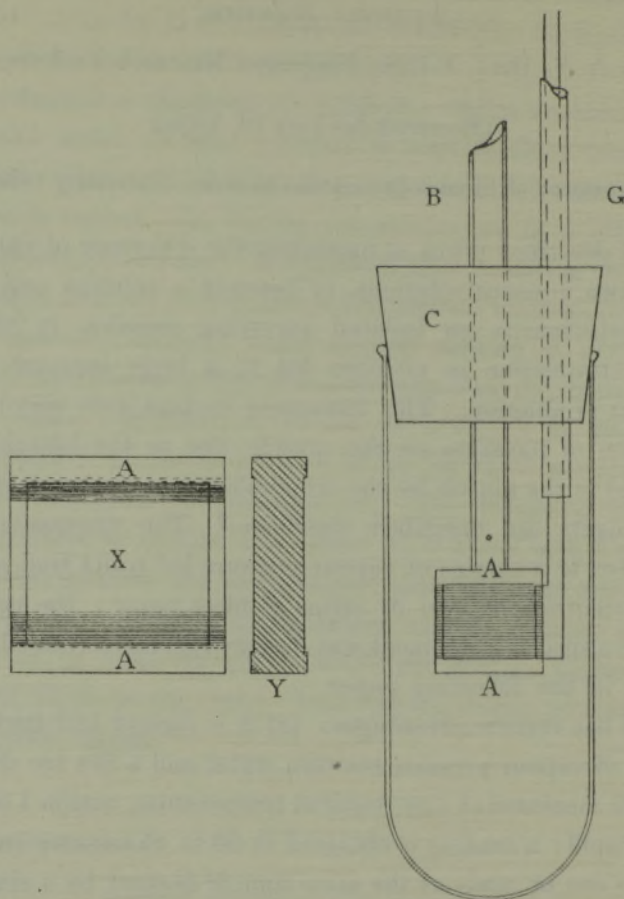
### *Apparatus.*

The thermopile shown in the figure is symmetrical; it has one set of junctions in a line down the middle of one face, the other set in a similar line down

\* 'Roy. Soc. Proc.,' B, vol. 105, p. 298 (1929) and *ibid.* (in preparation).

† That is, the difference of vapour pressure is measured directly and not obtained by subtraction of two separate measurements.

the middle of the opposite parallel face. It is wound upon a hollow brass rectangular frame insulated with "bakelite" varnish. The elements are of



Vapour Pressure Thermopile in Chamber. X, insulated brass frame shown enlarged and partly wound with wire; Y side view of same. AA, line of junctions. B, brass tube. C, rubber stopper. G, glass tube carrying leads to galvanometer. Dimensions of thermopile  $23 \times 23 \times 6$  mm.; wound with 71 turns of 38 S.W.G. constantan wire, half of each turn being electroplated.

silver-constantan, made by electroplating constantan wire as suggested by Hamilton Wilson.\* The wires should be wound as regularly and as close together as possible, and should cover the whole of each face of the frame. They are insulated by "bakelite" varnish, each coat of which requires careful baking to harden it and render it insoluble. During the baking a little hole in the frame is left open, afterwards this is sealed with shellac. Each face is

\* 'Proc. Phys. Soc.,' vol. 32, p. 326 (1920).



finally trimmed up with flaked or dissolved shellac, and the whole instrument is dipped for a few seconds into a mixture of melted paraffin wax and bees'-wax, to render it waterproof by a thin film over its surface. The thermopile is not unlike that employed for measuring the heat production of nerve,\* but simpler and more robust. Fuller details for constructing such instruments are given elsewhere.†

The thermopile is mounted on a brass tube, which passes through a rubber stopper; it is covered during use by a glass tube forced on to the stopper. The leads pass out through a glass tube to two copper terminals on a vulcanite platform above. A small hole is drilled at the thermopile end of the brass tube, to allow pressure equalisation to occur with the outside.

On one face (A) of the thermopile is laid a small strip of filter paper of suitable size dipped in solution (a); on the other face (B) a similar strip of filter paper dipped in solution (b). The chamber is kept moist by covering its walls with a large strip of filter paper dipped in any solution (c). Let  $p_a$ ,  $p_b$ , and  $p_c$  be the water vapour pressures of the three solutions. Then the solution (c) being in large excess, the water vapour pressure in the chamber will approximate to  $p_c$ , except in the immediate neighbourhood of faces A and B. The rate of condensation of moisture, therefore, on face A is equal to  $k(p_c - p_a)$ , where  $k$  is some constant depending on (i) the instrument, (ii) the temperature, and (iii) the barometric pressure. Similarly the rate of condensation of moisture on face B is  $k(p_c - p_b)$ , the  $k$  being the same since the instrument is symmetrical. Now owing to the condensation of water on the two faces of the thermopile the temperatures of these tend to rise above that of the surroundings. After a few minutes the tendency is balanced by heat loss, due to conduction, etc., and a steady state is reached in which face A attains a temperature  $k'(p_c - p_a)$  above the surroundings, and face B a temperature  $k'(p_c - p_b)$  above the surroundings, the constant  $k'$  depending (like  $k$ ) upon the instrument, the temperature and the pressure. The final *difference* of temperature, therefore, between face A and face B is  $k'(p_b - p_a)$ , and is independent of the vapour pressure of solution (c). Thus the E.M.F. developed in the thermopile is  $K(p_b - p_a)$  where  $K$  is a constant (which can be determined for any given instrument by calibration with solutions of known vapour pressures, but depends upon temperature and pressure) and  $p_a$  and  $p_b$  are the vapour pressures of the two solutions on the faces of the thermopile.

A large water bath is employed, stirred with an air stream and kept auto-

\* Downing and Hill, 'Roy. Soc. Proc.,' B, vol. 105, p. 147 (1929).

† Hill, 'Roy. Soc. Proc.,' B, vol. 103, p. 117 (1928).

matically at a temperature in the neighbourhood of  $20^{\circ}$  C. by a large gas regulator. The jet from which the gas emerges is ground off at an angle so that the mercury rising in the tube of the regulator in response to a rise of temperature of the bath diminishes the gas supply gradually. There is no "off" and "on" but continuous adjustment. The temperature, read by a Beckmann thermometer graduated in  $0.002^{\circ}$ , remains constant all day long within  $0.001^{\circ}$ . It is found that the reading due to two given solutions on the faces of the thermopile is approximately doubled by a rise of  $10^{\circ}$ . This implies a 7.2 per cent. increase per  $1^{\circ}$ , a 0.007 per cent. increase per  $0.001^{\circ}$ . The temperature regulation, therefore, is more than sufficient. It is desirable, however, to have it as good and as steady as possible, since sudden changes of temperature—even small ones—produce appreciable disturbances in the readings.

The difference of temperature between the two faces due to their unequal rates of evaporation (or condensation) is small, but still sufficient to reduce the difference of vapour pressure between the two solutions on them to a just perceptible degree. This, of course, does not affect the accuracy, which depends upon direct calibration with solutions of known vapour pressure. For example, a 1 per cent. NaCl solution on one face, against water on the other, gives a reading at  $20^{\circ}$  C. with thermopile No. 1 of about 12 microvolts. This instrument has 71 couples of electroplated silver-constantan, each giving (say) 35 microvolts per  $1^{\circ}$  C., a total of about 2500 microvolts per  $1^{\circ}$  C. Thus the 12 microvolts due to the difference between 1 per cent. NaCl and water betokens a temperature difference of about  $0.0048^{\circ}$  C. This corresponds to a relative change of vapour pressure of 0.000340 ( $0.00007$  per  $0.001^{\circ}$ ) which is about 6 per cent. of the difference between water and the NaCl solution. A corresponding relation exists for other concentrations.

The rate of dilution of the solution on the face of the thermopile, by the condensation of vapour on it, is not so great, except when large differences of vapour pressure exist in the chamber, as to produce any considerable effect during the time necessary to obtain a reading. It is possible, in any case, to avoid such dilution when measuring the difference of vapour pressure between a solution and water, by placing on the wall of the chamber either the solution itself or another solution judged to be approximately isotonic with it. Practically no evaporation of, or condensation on, the experimental solution will then occur, while the gradual evaporation of water from the opposite face is found to produce no effect on the reading until the filter paper has become perceptibly drier; this takes several hours to occur. It is often con-



venient, and accurate, to work differentially, *i.e.*, to measure the small difference between the experimental solution (*a*) (*e.g.*, blood) and a known solution (*b*) (*e.g.*, 0.96 per cent. NaCl) approximately isotonic with it. In that case the same solution (*b*) can be placed on the wall, and no perceptible dilution or concentration will occur on either face during the attainment of a reading. The only error of importance, due to evaporation, is caused by delay in placing the strip of wet filter paper on the face of the thermopile and mounting the latter in its chamber; in a hot dry room this error might be considerable if the time taken were too long. It is advisable to prepare everything beforehand, and to be as quick as possible in the final stages of laying the strip of filter paper containing the experimental solution on the face of the thermopile and of placing the cover in position.

The chamber should be connected to the atmosphere by a small hole or a narrow pipe. Initial temperature differences due to handling, etc., while setting up the apparatus, and the process of forcing the cover on to the stopper, may otherwise cause the pressure in the chamber to settle down finally to some unknown and arbitrary value. Mr. B. Topley, of the Department of Chemistry, University College, informs me that the reading should be inversely proportional to the total pressure in the chamber, provided that it depends mainly on diffusion, as it probably does; thus a constant pressure is necessary. The changes of barometric pressure which occur from day to day, or even during a single day, may be allowed for approximately by assuming—what has not yet been verified experimentally—the inverse relationship referred to above; or their effects can be eliminated by standardising the apparatus, or a similar one, on the day of the experiment by an observation made on a solution of known vapour pressure.

The galvanometer employed has been a Zernicke moving coil instrument (Ze) by Messrs. Kipp en Zonen of Delft, Holland, reading (at  $2\frac{1}{2}$  m. distance) to  $1.5 \times 10^{-10}$  amp. Except when the readings have been very small they have not been made directly on the scale, but by a null method employing a Pye rotary potentiometer led off into a 1 : 3000 potential divider constructed with copper wire. The arrangement was calibrated with an accurate potentiometer.

#### *Standards.*

The instrument described does not give absolute readings of the vapour pressure; it is necessary to calibrate it on a solution of known vapour pressure. The best available data appear to be those of Berkeley, Hartley and Burton\*

\* 'Phil. Trans.,' A, vol. 218, p. 295 (1919).

on cane sugar. Assuming (i) the results obtained at 30° C. with "Apparatus D," as corrected by Berkeley (*loc. cit.*, p. 347); (ii) the results obtained at 0° C. (*loc. cit.*, p. 344); and (iii) a value of the relative molal depression of vapour pressure of 0.0180 for very dilute solutions,\* two curves for the relatively molal depression were constructed for 0° C. and 30° C. respectively. The data employed are as follows:—

	Concentration: g. cane sugar per 100 g. water.							
	0	34	56.5	81.2	112	141	183	217.5
$\frac{p_0 - p}{[S] p_0} \times 10^2$ at 0° C.	[1.800]	—	2.094	2.207	2.344	2.456	2.558	2.602
$\frac{p_0 - p}{[S] p_0} \times 10^2$ at 30° C.	[1.800]	1.921	—	2.151	—	2.372	2.476	—

Here  $p_0$  is the vapour pressure of water and  $p$  that of the solution, while  $[S]$  is the concentration of sugar in g.-molecules per 1000 g. of water.

The curves for 0° C. and for 30° C. differ appreciably, but not considerably, from one another, so that a linear interpolation between them is allowable. The interpolated data for 20° C. are as follows:—

Table I.

	Concentration : g. cane sugar per 100 g. water.						
	0	10	20	30	40	50	60
$\frac{p_0 - p}{[S] p_0} \times 10^2$	1.800	1.845	1.890	1.935	1.980	2.025	2.070
	70	80	90	100	110	120	130
$\frac{p_0 - p}{[S] p_0} \times 10^2$	2.115	2.160	2.204	2.247	2.288	2.328	2.365
	140	150	160	170	180	190	200
$\frac{p_0 - p}{[S] p_0} \times 10^2$	2.398	2.427	2.454	2.477	2.497	2.515	2.530

\* This theoretical number is justified experimentally, at least at 0° C., by freezing point measurements made on dilute solutions of cane sugar (see Bedford, 'Roy. Soc. Proc.,' A, vol. 83, p. 459 (1910)) which allow the calculation of the identical value.



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If desired sodium chloride solutions can be used instead of cane sugar as standard. Data contained in the 'International Critical Tables,' vol. 3, allow us to interpolate the following smoothed values for a temperature of 20° to 25° C.

Table II.

	Concentration : g. NaCl to 100 g. water.						
	0.5	1.0	1.5	2.0	2.5	3.0	3.5
$\frac{p_0 - p}{[S] p_0} \times 10^2$	3.317	3.285	3.275	3.269	3.267	3.268	3.270
	4.0	4.5	5.0	6.0	7.0	8.0	9.0
$\frac{p_0 - p}{[S] p_0} \times 10^2$	3.273	3.278	3.285	3.302	3.320	3.339	3.359
	10.0	11.0	12.0	13.0	14.0	15.0	
$\frac{p_0 - p}{[S] p_0} \times 10^2$	3.380	3.401	3.423	3.447	3.471	3.495	

These values were found to be in good agreement with those given above for cane sugar.\* A similar set of data for KCl gives the following smoothed interpolated values, the effect of temperature being stated to be negligible.

\* The results for NaCl published by Bousfield ('Roy. Soc. Proc.,' A, vol. 103, p. 429 (1923)) appear to be considerably in error, if we accept the calibration with cane sugar as correct, see below.

Table III.

	Concentration : g. KCl per 100 g. water.						
	0.5	1.0	1.5	2.0	2.5	3.0	3.5
$\frac{p_0 - p}{[S] p_0} \times 10^3$	3.319	3.251	3.220	3.203	3.191	3.183	3.177
	4.0	4.5	5.0	6.0	7.0	8.0	9.0
$\frac{p_0 - p}{[S] p_0} \times 10^2$	3.173	3.169	3.167	3.163	3.161	3.159	3.158
	10.0	11.0	12.0	13.0	14.0	15.0	
$\frac{p_0 - p}{[S] p_0} \times 10^2$	3.158	3.159	3.161	3.163	3.165	3.168	

These again, so far as they have been tested, have been found to be in good agreement with those for cane sugar and for NaCl.

#### *Accuracy.*

Random errors, at present uncontrollable, perhaps due to variations in setting up, appear to affect the readings, on the average to about  $1\frac{1}{2}$  per cent. with not too dilute solutions. An early trial in which a solution of cane sugar, 5 g. to 100 g. water, was compared several times with water, led to the following series of readings on the galvanometer scale :—

No. ....	1	2	3	4	5	6
Reading, mm. ....	608	605	606	604	601	602
Constant after, minutes ....	30	35	52	31	33	60

The agreement is unusually good, but shows what may sometimes be attained. The tests shown in Table IV, carried out at various times, give a fairer impression of the average accuracy.



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Table IV.—In this table percentage concentrations are given as grammes of solute to 100 grammes of water; molal concentrations as gramme-molecules to 1000 grammes of water. Readings are given as turns of the rotary potentiometer (in the last experiment as millimetres on the scale).

*Experiment of December 16, 1929—*

NaCl 1 per cent. *versus* water gave 9.29 turns.

NaCl 6 per cent. *versus* water gave 55.50 turns.

Ratio :—Observed, 5.98; from Table II, 6.03.

*Experiment of December 17, 1929—*

Number .....	1	2	3	4
Cane sugar, per cent. ....	10	60	—	—
NaCl, per cent. ....	—	—	1	6
Reading <i>versus</i> water .....	9.57	65.18	9.63	58.33

The ratio of reading (2) to reading (1) is 6.81; from Table I, 6.73.

The ratio of reading (4) to reading (3) is 6.06; from Table II, 6.03.

The ratio of reading (4) to reading (2) is 0.89; from Tables I and II, 0.93.

*Experiment of December 18, 1929—*

(a) NaCl 1 per cent. *versus* cane sugar 10 per cent.

Ratio :—Observed, 1.036; from Tables I and II, 1.042.

(b) NaCl 6 per cent. *versus* cane sugar 60 per cent.

Ratio :—Observed, 0.917; from Tables I and II, 0.933.

*Experiment of December 21, 1929—*

NaCl 0.25, 1 and 6 per cent. *versus*, respectively, cane sugar 2.5, 10 and 60 per cent.

Ratios :—Observed, 1.17, 1.06 and 0.90; from Tables I and II, —, 1.04 and 0.93.

*Experiment of December 30, 1929—*

Number .....	1	2	3	4	5	6
Cane sugar, per cent. ....	60	—	—	—	—	10
NaCl, per cent. ....	—	—	6	—	1	—
KCl, per cent. ....	—	10	—	—	—	—
Glucose, per cent. ....	—	—	—	10	—	—
Reading <i>versus</i> water .....	63.00	75.35	60.50	17.82	10.01	10.13

Ratio :—

Reading (1) to (6) : Observed, 6.21; from Table I, 6.73.

Reading (3) to (5) : Observed, 6.04; from Table II, 6.03.

Reading (2) to (3) : Observed, 1.244; from Tables II and III 1.249.

Reading (3) to (1) : Observed, 0.96; from Tables I and II, 0.93.

Readings (4) and (1) lead to a molal relative depression of 0.0185 for 10 per cent. glucose. There are no data for glucose in the 'International Critical Tables,' but, if glucose and cane sugar may be compared, Table I gives for a solution of the latter of equivalent strength 0.01885.

*Experiment of December 31, 1929—*

NaCl 6 per cent. and 1 per cent. *versus*, respectively, cane sugar 60 per cent. and 10 per cent.

Ratios :—Observed, 0.924 and 1.067; from Tables I and II, 0.93 and 1.042.

*Experiment of January 2, 1930.—Comparison of NaCl 1 M. and KCl 1 M.*

Face A .....	NaCl	KCl	Water
Face B .....	KCl	NaCl	NaCl
Reading: turns .....	-2.45	+2.45	+59.3

$$\text{V.P. depression KCl} = 1 - \frac{2.45}{59.3} = 0.959.$$

For 1 M. solutions Tables II and III give a ratio of 0.957.

Table IV.—(continued).

*Experiment of January 3, 1930—Comparison of CaCl<sub>2</sub> 2M/3 and NaCl 1 M.*

Face A .....	NaCl	CaCl <sub>2</sub>	Water
Face B .....	CaCl <sub>2</sub>	NaCl	NaCl
Reading: turns .....	+0.80	-1.80	+58.6
V.P. depression CaCl <sub>2</sub>	$= 1 + \frac{1.3}{58.6} = 1.022.$		
V.P. depression NaCl			

There are no data in the Tables for CaCl<sub>2</sub> to check this comparison.*Experiment of January 6, 1930, and January 7, 1930.—Comparison of 1 per cent. NaCl and 10.404 per cent. cane sugar; these, from Tables I and II, should be isotonic. The experiment was set up anew 10 times in succession, as follows:—*

Face A .....	Water	NaCl	C.S.	NaCl	C.S.	NaCl
Face B .....	NaCl	C.S.	NaCl	C.S.	NaCl	C.S.
Reading, mm. ....	+1223	-1	+14	+16	-20	-8
Ratio: NaCl/C.S. ....	—	1.001	1.011	0.987	0.984	1.007
Face A .....	C.S.	NaCl	C.S.	NaCl	C.S.	
Face B .....	NaCl	C.S.	NaCl	C.S.	NaCl	
Reading, mm. ....	+4	-34	-32	-36	+16	
Ratio: NaCl/C.S. ....	1.003	1.028	0.974	1.029	1.013	

Mean value of ratio 1.004.

Average divergence from mean  $\pm 0.014$  or 1.4 per cent.*Discussion.*

The principle of the method described above is clearly nothing but that of the wet-bulb thermometer, increased in sensitivity. It is interesting to record that A. W. Reed\* in 1913 demonstrated the lowering of vapour pressure of a solution by two wet-bulb thermometers, moistened with a sodium chloride solution and with water respectively. Reed used ordinary thermometers and gave no quantitative results.

Other methods of measuring the depression of vapour pressure in small quantities of solutions have been described, *e.g.*, by Barger and by Whytlaw-Gray and Whitaker.† These have their advantages for special purposes. The present method has, up to the present, been used only for aqueous solutions. For solvents other than water it will be necessary to test, and perhaps to modify, the insulation of the thermopile. One possible difficulty, which was expected, has not hitherto been encountered, *viz.*, the adsorption of the solute by the filter paper; it would clearly be possible to avoid the effect of this on the vapour pressure by leaving the filter paper for a long time in an excess of the solution to come into equilibrium with it. When this has been done no effect on the reading has been noticed with the solutions employed.

\* 'Chem. News,' vol. 107, p. 64 (1913).

† Barger, 'Trans. Chem. Soc.,' vol. 85, p. 286 (1904); Whytlaw-Gray and Whitaker, 'Leeds Phil. Soc. Proc.,' vol. 1, p. 97 (1926).



If the method proves to be useful for more dilute solutions, or to a higher degree of accuracy, the possible effects of adsorption must be further examined.

By increasing the number of observations and taking a mean, as in the last experiment of Table IV, it is clearly possible to attain a greater accuracy than by a single observation. That experiment shows clearly that the data of Tables I and II, for cane sugar and for sodium chloride respectively, are in close agreement. Accepting the value for the molal relative depression of cane sugar as correct, that for sodium chloride (1 g. to 100 g.  $\text{H}_2\text{O}$ ) is calculated to be 0.0330. Interpolated from the data in the 'International Critical Tables' it should be 0.03285. The value calculated from the data of Bousfield and Bousfield is 0.0359, which is apparently in error to the extent of nearly 9 per cent. The value for sodium chloride, 6 g. to 100 g.  $\text{H}_2\text{O}$ , calculated from the results of Table IV, assuming the value 0.0330 for 1 g. to 100 g.  $\text{H}_2\text{O}$  to be correct, is 0.0330; or, assuming the value for 60 g. cane sugar to 100 g.  $\text{H}_2\text{O}$  to be correct, 0.0332. The value interpolated from Bousfield and Bousfield is 0.03425, which is  $3\frac{1}{2}$  per cent. greater than the mean of these. Bousfield and Bousfield measured vapour pressure directly as pressure, a procedure which is apparently more liable to error than the weighing of the losses by evaporation from solution and solvent respectively when brought into equilibrium with the same slow stream of air (Berkeley, Hartley and Burton).

### *Summary.*

A thermoelectric method is described by which the difference of vapour pressure between two solutions, or between a solution and the pure solvent, can be measured. The principle involved is simply that of a differential wet-bulb thermometer of high sensitivity. A reading is obtained in 30 to 45 minutes and the average error of a single observation is of the order of  $1\frac{1}{2}$  per cent. of the difference read.

My thanks are due to Mr. A. C. Downing for the construction of the thermopile employed.