

Citation:

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TABLE II.

Temperature.	Duration of measurements	Rise of level in mm.	Rise of level in mm. per hour
68.0	2 $\frac{1}{3}$	- 15	- 6
75.0	1 $\frac{1}{2}$	+ 46	+ 30
72.0	$\frac{5}{6}$	+ 14	+ 17
70.0	5 $\frac{1}{4}$	+ 10	+ 2
69.5	58	+243	+ 4
69.5	31	- 36	- 1

At *constant* temperature (69°.5) the direction of motion of the meniscus has changed. This change proves that also in this case there are more than two modifications present at the same time.

5. How extraordinarily marked the retardations are which may occur, is shown by the behaviour of a sample Cu_{IV} (comp. § 7 of our first paper); it was not possible to "bring it into motion" even after treating it with a solution of copper sulphate. However, it ought to be pointed out that there was no finely divided powder present, which was the case with the other samples we investigated.

Utrecht, April 1914.

VAN 'T HOFF-Laboratory.

Botany. — "*Energy transformations during the germination of wheat-grains*". By LUCIE C. DOYER. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of April 24, 1914).

The reserve materials of seeds represent a large quantity of chemical energy. In germination these substances are split into compounds with a much smaller number of atoms and partly by the process of respiration completely oxydized to carbon dioxide. In consequence of these exothermic processes a considerable quantity of energy is set free, which can be used for the various vital-processes.

In order to obtain a conception of these transformations of energy during germination, I have made some observations on germinating

wheat-grains, on which I now wish to make a short preliminary communication.

The germination of the wheat-grains under observation always took place at about 20° C. in the dark, there could therefore be no energy taken up from without by assimilation of carbon dioxide; all the energy needed for the processes of germination had therefore to be provided by means of the reserve materials.

At the commencement of germination imbibition chiefly takes place, in this way heat is already liberated, therefore energy; then there follow very soon a series of exothermic processes, in wheat-grains more especially decomposition of starch to sugars and complete oxydation of this material of respiration to carbon dioxide. The energy set free in this manner is now applied to various ends: 1st. for all kinds of synthetic processes by means of which plastic materials are formed for the growing plant, 2nd. for the production of osmotic pressure, 3rd. for the overcoming of internal and external resistances, and 4th. energy is given off in the form of heat-radiation.

The methods used to obtain an insight into these various energy-relations were the two following:

1st. Determination of the heat of combustion before germination, and after the germination had been progressing for some time.

2nd. Determination of the quantity of heat produced during germination.

As regards the first point, it must be pointed out that the internal chemical energy during a certain length of germination must decrease; a measure of this loss can be found by determining the difference in the heat of combustion. The energy which will no longer be shown by this heat of combustion, is that which is utilized osmotically, for overcoming resistances and which is lost by the giving out of heat. The energy, however, which is used up during germination for synthetic processes is again fixed as chemical energy and is indeed represented by the heat of combustion.

The loss of energy, that is found by determinations of the heat of combustion, does not give therefore the total amount of energy, which has played a part during germination, for a considerable part of this energy has again been withdrawn from observation by the synthetic processes.

The BERTHELOT-bomb was used for determining the heat of combustion. In it a weighed quantity of wheat-grains, germinated or ungerminated and previously dried for a long time at 100°, were burnt; by the rise of temperature of the water in which the bomb

was placed, in combination with the water-value of the respective parts, the amount of energy which was set free by combustion, could be calculated.

This heat of combustion was always calculated for the weight of 1 gram of ungerminated wheat (initial-weight); this was done in the case of both germinated and ungerminated wheat. In this way comparable values were obtained; the difference in heat of combustion after a definite period of germination gave therefore the loss of energy above referred to.

Heat of combustion of wheat calculated per gram of the initial-weight, expressed in gram-calories.

The germination took place at $\pm 20^{\circ}$ C.		Average values	Loss of energy
Ungerminated	3748—3774—3778—3794—3797 ¹⁾	3778	
After 1 day's germin:			4 1st day
" 2 " "	3756—3793	3774	4 2nd day
" 3 " "	3740	3740	34 3rd day
" 4 " "	3653—3681—3682—3707—3707	3686	54 4th day
" 5 " "	3594	3594	92 5th day
" 6 " "	3498	3498	96 6th day
" 7 " "	3318	3318	180 7th day

It is clear from these values, which were found for the heat of combustion, that the loss of energy during germination steadily increased. The loss of energy in the first two days was slight; probably imbibition had chiefly taken place at this stage, whilst the chemical transformations had then only subsidiary importance.

It can be further deduced from the figures that between the 2nd and 3rd day especially the loss of energy greatly increased, and after that continued to rise.

If these values for the loss of energy after different lengths of germination are summarized graphically, a curve is obtained, which begins almost horizontally, and rises more and more steeply.

The loss of energy per hour per kilogram of initial-weight can be roughly calculated from the loss of energy during the different days. The loss of energy per gram of initial-weight was after two days 4 calories.

¹⁾ The figures are arranged in ascending values, and not chronologically.

During the 1st and 2nd days the loss of energy per hour per kilogram of the initial-weight was therefore roughly $\frac{1000}{48} \times 4 = 83$ cal.

The same for the 3 rd day	$\frac{1000}{24} \times 34 = 1417$	„
„ „ „ „ 4 th „	„ $\times 54 = 2250$	„
„ „ „ „ 5 th „	„ $\times 92 = 3833$	„
„ „ „ „ 6 th „	„ $\times 96 = 4000$	„
„ „ „ „ 7 th „	„ $\times 180 = 7500$	„

This amount of lost chemical energy corresponds therefore in all probability to that which is applied to osmotic purposes, to the overcoming of resistances and to the evolution of heat.

In a second series of observations I also attempted to determine directly the amount of heat that is given off. The principle, that underlay these determinations, was briefly as follows: air, saturated with water-vapour, which had been brought to a constant known temperature, was passed over germinating wheat-grains at a constant velocity, these acted as a continuous source of heat; the air which passed over it therefore rose in temperature.

If the difference of temperature between the air streaming in and out were measured, when the latter passed at a known rate, then in the ideal case when absolutely no other heat conduction took place, the amount of heat set free could be calculated from the known heat-capacity of the air. Moreover for this the space in which the seedlings were placed would have to be completely saturated with water-vapour; if this were not so, evaporation would take place on germination, in which way heat would be withdrawn from the observation.

The apparatus with which I conducted these experiments consisted of a copper vessel placed in a waterbath of constant temperature. Through this copper vessel, in which a large number of germinating wheat-grains were placed, a current of air was directed at the rate of 3 litres per hour; the air had had for a large part of its course an opportunity to take up the constant temperature of the water. A set of thermal needles served to measure the difference between the temperatures of the air entering and leaving; the current resulting from this difference in temperature was led through a very sensitive mirror-galvanometer, whilst a spot of light was thrown by the mirror on a scale and so made it possible to compare accurately the deflections.

The apparatus was for the most part composed of materials which

conduct heat very easily, thus making the ideal case described above very far from being realised.

If a source of heat were introduced into the vessel while a regulated stream of air was passed through, only a part of the heat liberated could be used to raise the air-temperature; the remainder would pass into the surrounding water by conduction.

It was to be expected that, when a definite source of heat was present, a maximum difference of temperature between the in- and out-streaming air would arise after some time; with the given rate of passage of the air this difference of temperature caused by this source of heat, could not become greater. A calculation as to how great this maximum difference of temperature would be for different amounts of heat, would be very complicated, if not entirely impossible. For this reason the simplest way was to calibrate the apparatus by introducing a source of heat of known magnitude. For this purpose a manganin-wire was placed inside the apparatus over as wide an extent as possible, in the place where later the germinating wheat-grains were to be put. This wire formed a metallic contact with two copper rods which projected above the lid of the apparatus. An electric current could be passed through the manganin-wire by connecting these rods with the two poles of an accumulator. The resistance of the manganin-wire was accurately determined, whilst a milliamperemeter, placed in the circuit, served to measure the strength of the current. By taking the current from 1, 2, and 3 accumulators alternately, sources of heat of different magnitude could be introduced into the apparatus.

When in this way a source of heat of known magnitude occupied the apparatus, air was passed through and at regular intervals the (double) deflection of the spot of light on the scale was read till this ultimately remained constant and therefore had reached a maximum. These observations were conducted at temperatures of 20°, 30°, and 40° of the surrounding water, and also therefore of the entering air.

These calibration-experiments showed: 1st that the maximum deflection of the spot of light, or in other words the difference of temperature between the in- and out-going air was roughly in proportion to the source of heat which was placed in the apparatus, 2nd that this proportionality was maintained at a surrounding temperature of 20°, 30°, and 40°, 3^d that the absolute magnitude of the deflection was independent of this temperature, 4th, that a deviation of 1 centimetre corresponded to a *development of about 11.5 calories per hour.*

As the apparatus was now calibrated it was possible conversely, by reading the deflection of the spot of light, to calculate the magnitude of any source of heat, which was in the apparatus. For such an unknown source of heat germinating wheat-grains were used. (The number of these was always 500).

In the course of the experiments however it became plain that in this case the deflection of the light spot could not be looked upon as showing exclusively the heat-evolution which took place in germination. For when 500 germinated wheat-grains, which had previously been killed by heating to 100° , were placed in the apparatus, then it was seen that the spot of light inevitably passed the zero; in various experiments of this kind a deflection of about 8 centimetres was always found.

In order to ascertain whether the dead seedlings did not after all give off some heat possibly as a result of a continued enzyme-action, the apparatus was filled by way of control with quantities of filterpaper previously soaked in water. In this case there could be no question of heat-evolution by the filterpaper. Also with this arrangement of the experiments the spot of light invariably passed the zero, reaching finally a maximum deflection corresponding to that obtained when dead seedlings were placed in the apparatus. The extent of this deflection was independent of the temperature of the surrounding water (fixed at 25° and 35°), in other words, with this arrangement of the experiment there arose always a constant difference of temperature between the in- and out-going current of air.

Since in these cases no direct evolution of heat by means of the substances used was possible, another cause for the rise of temperature in the experiment described had to be found. The most probable thing was that condensation of water-vapour must have taken place in some way and that the heat thus set free caused an increase of temperature in the out-going air and in consequence of this of the upper thermal needle. In the calibration-experiments the spot of light had remained at zero when there was no heat-source in the apparatus; the difference in conditions then and during the experiments just described was, that the space within was in the latter case for a great part filled with a completely imbibed mass.

The many efforts made to eliminate this irregularity were practically without results; I was therefore compelled, in experimenting with living seedlings, to adopt a correction, the amount of which was experimentally fixed while theoretically it had to be left partly unexplained.

Since it was therefore found that by filling the apparatus with

very moist substances a difference in temperature between the two needles arose when the current of air passed through, it had to be assumed that this would be also the case when living seedlings were present. The deflection found in that case would have to be attributed partly to this physical cause, partly to generation of heat which actually took place in germination. It was therefore necessary to subtract from the deflection found in this arrangement the amount of deflection found in the experiments with dead seedlings, the remainder then being the measure of the heat generated in germination. This latter was observed at different temperatures and in different stages of germination. In consequence of the complications mentioned higher up the sources of error were relatively very numerous and this was especially noticeable in the few parallel-determinations which were carried out, so that in the values summarized in the table below an approximation to the amounts of heat given off must be expected rather than an exact measure thereof. These influences are proportionately very large in the lower values.

Number of calories given off per hour calculated per kilogram
of the initial weight.

Temp.	On the 2 nd day of germination	On the 3 rd day of germination	On the 4 th day of germination	On the 5 th day of germination	On the 6 th day of germination	On the 7 th day of germination
20°		710	2143	2790		2869
25°	363	540	2938	2977 3455	4341	
30°			4999 6313	6790		
35°		752		7326	7575	
40°				5689	6847	

It appeared therefore from the values found that the generation of heat on the 2nd and 3rd days was still small in comparison to that in later stages of germination. The generation of heat shows a great and sudden increase between the 3rd and 4th day and it is probable that it continued to increase slowly during the following

days, but the relatively small differences from the 4th to the 7^h day justify the calculation of an average for this period of germination.

Number of calories given off per hour calculated per kilogram of the initial weight.

Temp.	On the 4 th day	5 th day	6 th day	7 th day	Average
20°	2143	2790		2869	2601
25°	2938	2977 3455	4341		3428
30°	4999 6313	6790			6034
35°		7326	7575		7450
40°		5689	6847		6268

The generation of heat, therefore, was much influenced by the surrounding temperature; by a rise of 10°, the quantity of heat evolved, increased to more than double. The generation of heat was diminished at 40°, a proof of the harmful influence of this temperature.

Finally a comparison can be made between the number of calories pro kilogram of initial weight given off as heat and the loss of energy deduced from the heat of combustion. This comparison could only be made for a temperature of 20° because at this temperature germination had always taken place, so that the heat of combustion referred to processes at this temperature only.

Loss of energy per hour per kilogram of the initial weight.

At 20°	By heat given off	Calculated from the heat of combustion
On the 2nd day		83 Cal.
" " 3rd "	710 Ca.	1417 "
" " 4th "	2143 "	2250 "
" " 5th "	2790 "	3833 "
" " 6th "		4000 "
" " 7th "	2869 "	7500 "

The total amount of chemical energy which was set free in germination was therefore always larger than the quantity of energy given off as heat to the surroundings. A part of the free energy which became available in the process of germination was therefore evidently used for other purposes (osmosis etc.) than for heat-evolution only.

This was however doubtful only on the second day, the evolution of heat on that day was not determined; the loss of energy, calculated from the heat of combustion, was however so small in this period that it is very possible that the evolution of heat at that moment, was larger. If afterward it should appear that this is really the case, it would be very intelligible. For in the beginning of germination imbibition will principally take place so that in this case evolution of heat is not at all necessarily connected with chemical transformations.

The results of this investigation may therefore be summarized as follows.

The loss of energy calculated from the heat of combustion as well as the evolution of heat increase with the duration of germination.

Both are small at the beginning of germination and greatly increase, chiefly on the 3^d day.

The evolution of heat is greatly dependent on the surrounding temperature.

The optimum of heat-evolution is roughly 35°.

The total loss of energy during germination at 20° exceeds the loss of energy by evolution of heat at the same temperature.

Utrecht, 1914.

Botanical Laboratory.

Chemistry. — "*Equilibria in ternary systems XV*". By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of April 24, 1914).

In our previous considerations on saturationcurves under their own vapourpressure and on boilingpointcurves we have considered the general case that each on the three components is volatile and occurs consequently in the vapour. Now we shall assume that the vapour contains only one or two of the components. Although we may easily deduce all appearances occurring in this case from the general case, we shall yet examine some points more in detail.