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lower temperature in the seeds with a higher protein content is perhaps connected with the fact that the optimum for proteolytic generally lies lower than for diastatic ones.

In conclusion I mention a few experiments with capitula of *Crepis biennis*. I only made observations from 30°—50°; at each of the temperatures employed a falling-off was observable, which was very marked and gave an almost straight line. The experiments are too few in number to allow of a definite conclusion being drawn but the marked decline is in this case also most probably influenced by a want of respiratory material. According to the observations the respiration increases during the first hour right up to 45°, while the temperature limit of life is only a very little higher; after a 6 hours' exposure to 45° the flowers were dead.

My results are therefore as follows:

1. the theory of BLACKMAN is also applicable to respiration to the extent that:

- a. the rule of VAN 'T HOFF-ARRHENIUS holds good from 0° to 20°—25°.
- b. the optimum may be displaced with the time of observation.
- c. the falling off at 40°, 45°, and 50° has a logarithmic course in seedlings.

2. the course of respiration depends very much on the nature of the reserve food.

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Chemistry. — "*On retrogressive melting-point lines.*" By Prof.

A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

(First Communication.)

Applying the method indicated by VAN DER WAALS¹⁾ we find for the melting-point line under the vapour pressure the following equation:

$$\frac{dx_L}{dt} = - \frac{1}{T} \left(\frac{\partial x_L}{\partial p} \right)_T \frac{(x_L - x_g) \{ (V_g - V_L)(Q_m + Q_{SL}) - (V_L - V_S)Q_{LG} \}}{(V_g - V_L) \{ x_L - x_g \} V_S - (x_S - x_g) V_L + (x_S - x_L) V_g}$$

in which Q_{SL} = mol. heat of melting of a compound of the concentration x_S ;

Q_m = differential mol. heat of mixing of the melted compound with a solution of the concentration x_L ;

Q_{LG} = mol. heat of evaporation of a solution of the concentration x_L .

¹⁾ Versl. Kon. Akad. v. Wet. 28 Febr. 1885 and Rec. Trav. chim. 5, 336 (1886).

x_S , x_L and x_g denote the concentration of the coexisting solid, liquid, and vapour phase, expressed in gr. mol. of the component B per one gr. mol. total, and V_S , V_L , and V_g indicate the mol. volumes of these phases.

If we now confine ourselves to the system $H_2O - Na_2SO_4$, and if we apply the above formula successively to the melting-point lines of $Na_2SO_4 \cdot 10 aq$, of rhombic Na_2SO_4 , and of monoclinic Na_2SO_4 , we arrive at remarkable results.

Starting with the melting-point line of $Na_2SO_4 \cdot 10 aq$, we must remark beforehand that for the case that no maximum or minimum occurs in the p - x -figure, which is here excluded, $\left(\frac{\partial x}{\partial p}\right)_T$ is always negative.

As now the denominator is already positive some degrees below the melting point in consequence of the predominating value of $(x_S - x_L)V_g$, the sign of $\frac{dx_L}{dt}$ will be further governed by the numerator, and so we see that it follows from the positive values of $\frac{dx_L}{dt}$ for the melting-point line of $Na_2SO_4 \cdot 10 aq$ that the numerator, so the sum of the caloric quantities, is positive there.

This is the usual case, and does not call for further remarks.

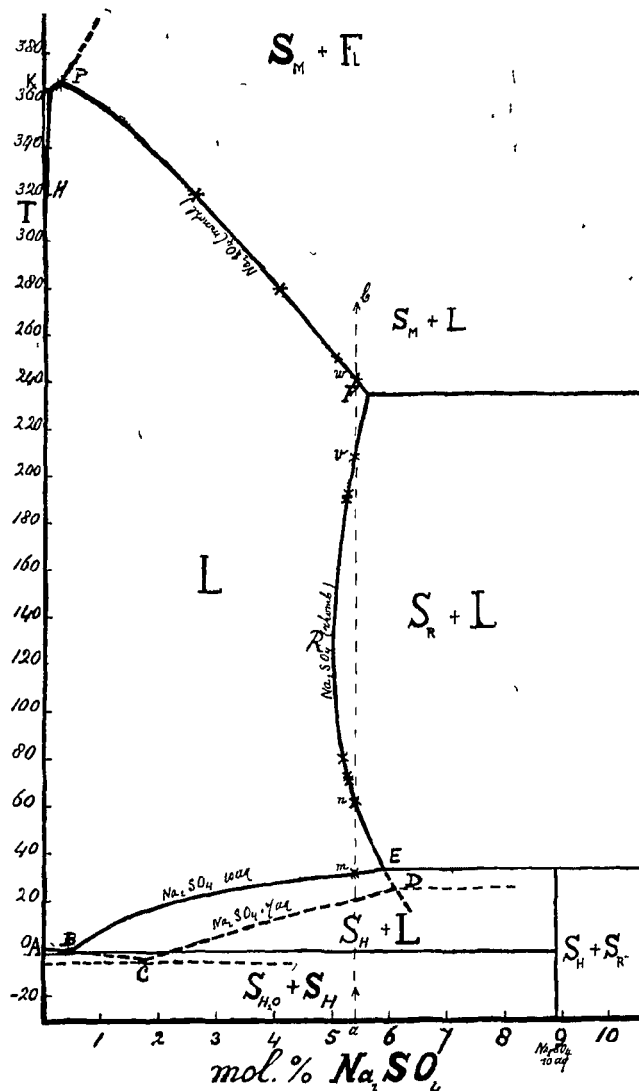
From the figure p. 229, which represents the projection of the three-phase regions $S_B + L + G$ on the T, X -plane we see, however, that the melting-point line of the rhombic Na_2SO_4 , which becomes stable in E presents the particularity of at first retrograding, and now the question suggests itself, how this behaviour can be accounted for.

When in a solution the phenomenon of hydration takes place, the differential heat of mixing, which is on the whole thermodynamically positive, can become negative, because the formation of hydrate is usually attended with generation of heat.

Now it is clear from the above equation that the melting-point line can become a retrogressive one only when the numerator with the caloric quantities has become *negative*, which will be the case when Q_m assumes a predominantly large *negative* value.

If we now consider the transition point E , we know that the solution, which coexists there with solid $Na_2SO_4 \cdot 10 aq$, is also in equilibrium with rhombic, anhydrous Na_2SO_4 . Now if this solution is hydrated, as is made probable by various phenomena, it is clear that the differential heat of mixing of anhydrous Na_2SO_4 must be much greater than that of $Na_2SO_4 \cdot 10 aq$, as the molecules, before

being solved have already been hydrated to a certain extent in the latter case. In consequence of this Q_m can have become so strongly



negative that it predominates over the other positive caloric quantities, of which Q_{SL} now relates to the anhydride.

So, seen in this light, we may expect that if a hydrate splits off much water at its transition point, a retrograding melting point line will arise, because then the probability that the change in the heat of melting is smaller than that in the heat of mixing, is very great.

From the T,X-figure it appears further, that the retrogression of the melting-point line of rhombic anhydrite becomes less and less

at higher temperature, so that $\frac{d\omega_L}{dt}$ passes through zero at the point R , after which it assumes again positive values.

This peculiar phenomenon can hardly be explained in another way than by assuming a retrogression of the hydration in solution with rising temperature, which causes the heat of mixing to become smaller negative, so that the denominator of the fraction first becomes zero and then again positive.

This continues like this up to the transition point F , where another remarkable phenomenon is met with. In this point, where the rhombic modification passes into the monoclinic one, which is a transformation without splitting off of water, arises a strongly retrograding melting-point line too. Now, as the difference of state between rhombic and monoclinic Na_2SO_4 disappears in the liquid state, we know with certainty that the heat of mixing of the two melting-point lines, is exactly the same in the point F , from which follows that the reversal of sign of $\frac{d\omega_L}{dt}$ must be attributed to the circumstance that

Q_{SL} now refers to the monoclinic modification, the heat of melting of which must be considerably smaller than that of the rhombic form.

If we now proceed to higher temperature, complications appear, as we now approach the critical state, in which $V_G - V_L$ and Q_{LG} become continually smaller, till they finally become zero in the critical point.

In this point $\left(\frac{\partial \omega_L}{\partial p}\right)_T = -\infty$, so that $\frac{d\omega_L}{dt}$ becomes $= -\infty$.

In conclusion we may still remark that it follows from this consideration that the hydration continues to exist even at the critical temperature.

If we now further consider that it follows from my investigation of the system ether-anthraquinone that a partly retrogressive melting-point line must exist also there, the supposition suggests itself that the whole phenomenon is in connection with the formation of compounds in solution, but it is exactly the case ether-anthraquinone that admonishes us to caution, because nothing is known of a compound between these two substances in solid state. So it seems better to me to assume that the molecules of the two substances approach each other very closely in solution, leaving undecided whether this state can be called a compound or not.

Amsterdam, Sept. 1909.

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