approach each other between 50 and 60% I. This case, therefore, is similar to the behaviour of the mixtures of Cl and S studied some time ago [1]), with this difference that for the composition S_2Cl_2 the lines nearly came into contact, whilst in this case the distance remains much greater.

The peculiar form of the boiling lines points, however, to the existence of combined molecules of the two elements. Whether these answer to the formula Br I cannot be decided from the form of this line, but perhaps better from the p,x-lines which will be studied afterwards.

Below the line ADB the region of the liquids is situated. These on further cooling deposit solid phases. These phenomena are represented by the two lines EFG and EHG. The second line shows the initial and the first line the final solidifying points. They form two continuous lines which however come into contact at 50 atom percent I.

A similar type of solidification points as a rule to mixed crystals.

The equality of the composition of liquid and solid at the concentration Br I — without this point being a maximum or a minimum — could, however, only be explained by assuming that Br I is a chemical compound.

Possibly this is the case, which has never as yet been satisfactorily proved, where a compound is mixable with both its components. We will endeavour to elucidate this matter by a determination of the density etc.

Chemistry. — "*On the action of emulsin.*" By Dr. R. O. HERZOG. (Communicated by Prof. C. A. PEKELHARING).

(Communicated in the meeting of October 31, 1903).

1. If we mix a solution of canesugar with invertin and determine the quantity inverted in definite times at a constant temperature, it appears that the inversion does not proceed as a reaction of the first order $\left(k = \frac{1}{t} l. \frac{a}{a-x}\right)$, the "constants" calculated from this equation increasing continuously during the period of the inversion. This might be explained by the increasing activity of the enzyme or by the influence exerted by the invert sugar formed.

V. HENRI [2]) has shown in an exhaustive paper that the latter is the cause and that the reaction proceeds according to the law

[1]) These Proc. June 1903.

[2]) Zeitschr. für physikalische Chemie **39**, 194 (1901).

regulating the unimolecular reaction where the products of reaction act (positively) autocatalytically.

For a similar case, OSTWALD [1]) has given the equation of reaction:

$$\frac{dx}{dt} = (k_1 + k_2 x)(a-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we integrate this equation and take $x = 0$, $t = 0$ we find:

$$\frac{1}{k_1+k_2a} l. \frac{a(k_2x+k_1)}{k_1(a-x)} = t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this equation a is the concentration at the beginning, x the amount of sugar inverted at the period t, k_1 and k_2 are the velocity constants. If we call

$$\frac{ak_2}{k_1} = \varepsilon. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we obtain the expression

$$k_1 = \frac{1}{t(1+\varepsilon)}. l. \frac{a+\varepsilon x}{a-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is more convenient for purposes of calculation.

In this particular case $\varepsilon = 1$, therefore for $a = 1$ $k_1 = k_2$.

Equation (4) now becomes:

$$2k_1 = \frac{1}{t} l. \frac{a+x}{a-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

2. If we measure the velocity of the emulsin action it appears that the "constants" of the logarithmic expression keep on decreasing as has already been stated by TAMMANN [2]).

As it appears from HENRI's experiments [3]) that the enzyme suffers no change, at least when the time of reaction is a short one, it was evident that the cause of the phenomenon was to be sought in a negative autocatalysis namely, *in the retardating influence of the products of inversion.*

In a similar case the equation of the reaction assumes, according to OSTWALD [4]) this form:

$$\frac{dx}{dt} = (k_1 - k_2 x)(a-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

After integration and calling $x = 0$ $t = 0$, we find:

[1]) Lehrbuch der allgemeinen Chemie. II, 2. 1 Teil. S. 264, 265.
[2]) Zeitschr. für physikalische Chemie **18**. p. 426 (1895).
[3]) Thèses P. 106. 107. (Paris 1903).
[4]) l.c. 271.

$$\frac{1}{k_1-ak_2} l.\frac{ak_2(k_1-k_2x)}{k_1(ak_2-k_2x)} = t \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If again we take

$$\frac{ak_2}{k_1} = \varepsilon . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

we find :

$$k_1 = \frac{1}{t(1-\varepsilon)} l.\frac{a-\varepsilon x}{a-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or

$$k_1(1-\varepsilon) = \frac{1}{t} l.\frac{1-\varepsilon\frac{x}{a}}{1-\frac{x}{a}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in which a is the concentration at the beginning, x the amount of sugar inverted in the period t, k_1 the velocity constant of the reaction if taking place without autocatalysis and k_2 the constant of the autocatalysis.

3. This formula was investigated in a number of cases and it appeared that the reaction may indeed, be represented by that expression.

As in the case of invertin it has appeared that the quantity ε, which, according to the assumption made, need only remain constant during the same series of experiments, as a rule suffers but little change (from 0 6 to 0.8). Probably, the value of ε depends on the previous history of the enzyme, but it should be remembered that emulsin is much more sensitive than invertin.

In the following tables

a stands for the concentration at the start

x the quantity inverted, therefore

$\frac{x}{a}$ the relative quantity inverted

t the corresponding time in minutes.

The third column contains the value of $k_1(1-\varepsilon)$ calculated according to (10).

In the fourth column we find $\varrho = \frac{1}{t} l.\frac{a}{a-x}$.

Experiments by V. HENRI [1]) on October 30, 1902

I.

0,14 N. Salicin solution $z = 0.6$.

$\frac{x}{a}$	t	$[(1-z)k_1]\,10^5$	$\rho \times 10^5$ [2])
0.132	25	[61]	246
0 209	55	80	185
0.306	87	81	182
0 534	211	78	157
0 603	271	76	148
0 686	375	73	135
0 950	1325	75	100

II

0.07 N. Salicin solution $z = 0.6$.

$\frac{x}{a}$	t	$[(1-z)k_1]\,10^4$	$\rho \times 10^5$
0 174	24	15	345
0 351	54	16	348
0 450	86	14	302
0 691	210	13	243
0 775	270	14	240
0.847	371	14	220

Experiments by V. HENRI on October 8, 1902.

I.

0,14 N. Salicin solution $z = 0.6$.

$\frac{x}{a}$	t	$(1-z)k_1]\,10^5$
0 110	31	[68]
0 305	123	53
0 447	211	58
0 516	276	56
0 583	343	56

II.

0.07 N. Salicin solution $z = 0.6$.

$\frac{x}{a}$	t	$[(1-z)k_1]\,10^4$
0.476	122	11
0 651	200	12
0.691	275	10
0 767	342	11

[1]) Thèses P. 108—109.

[2]) Calculated by HENRI l c. p. 103.

III.

0 035 N. Salicin solution $\varepsilon = 0.6$.

$\frac{x}{a}$	t	$[(1-\varepsilon)\,k_1]\,10^4$
0 182	28	13
0.564	121	15
0 685	208	13
0 818	275	16
0.879	341	17

Experiments by V. Henri on October 10, 1902.

I.

0 14 N. Salicin solution $\varepsilon = 0.8$.

$\frac{x}{a}$	t	$[(1-\varepsilon)\,k_1]\,10^5$
0 179	60	31
0 371	177	27
0 505	294	28
0.550	355	27
0 579	415	25

II.

0.105 N. Salicin solution $\varepsilon = 0.8$.

$\frac{x}{a}$	t	$[(1-\varepsilon)\,k_1]\,10^5$
0 216	60	39
0 402	176	37
0 606	293	40
0.636	357	36

III.

0.075 N. Salicin solution + 0 035 N. (Saligenin + glucose) $\varepsilon = 0$ 8.

$\frac{x}{a}$	t	$[1-\varepsilon)\,k_1]\,10^5$
0 157	57	28
0.400	172	32
0.539	291	31
0.597	355	32

IV.

0.105 N. Salicin solution + 0 035 N. (Saligenin + glucose) $\varepsilon = 0$ 8.

$\frac{x}{a}$	t	$[(1-\varepsilon)\,k_1]\,10^5$
0 128	59	22
0 344	176	25
0. 59	293	23
0 525	357	24

V.

0.07 N. Salicin solution + 0.07 N. (Saligenin + glucose $s = 0.8$)

$\frac{x}{a}$	t	$[(1-s)k_1]10^5$
0.146	57	25
0.327	173	23
0.376	292	[17]
0.536	355	25

VI.

0.7 N. Salicin solution $s = 0.8$.

$\frac{x}{a}$	t	$[(1-s)k_1]10^5$
0.221	58	41
0.524	172	50
0.688	291	55
0.712[1]	355	49

VII.

0.035 N. Salicin solution + 0.035 N. (Saligenin + glucose) $s = 0.8$.

$\frac{x}{a}$	t	$[(1-s)k_1]10^5$
0.194	57	36
0.469	170	42
0.618	289	42

VIII.

0.035 N. Salicin solution $s = 0.8$.

$\frac{x}{a}$	t	$[(1-s)k_1]10^5$
0.394	56	95
0.695	170	92
0.880	288	[136]

Experiment communicated by TAMMANN.
Zeitschr. fur physikalische Chemie. 18. 436.

3.007 gram Salicin in 180 cc water $s = 0.6$.

$\frac{x}{a}$	t[2]	$[(1-s)k_1]10^3$	$\rho \times 10^3$[3]
0.13	1	24	61
0.32	3	25	57
0.58	5	[38]	[75]
0.65	8	30	58
0.76	12	29	52
0.91	26	27	40
0.98	50	28	35

By way of comparison I cite an experiment with amygdalin which I have made in the course of another investigation.

[1]) In the original paper it says 0.612, but this is probably a mistake.
[2]) In hours.
[3]) Calculated by TAMMANN.

The hydrocyanic acid was titrated by LIEBIG's method; in the first period of the reaction, values are found corresponding with those of the sugar determination [1]).

0.1 N. Amygdalin solution.

$\frac{x}{a}$	t	$[(1-\frac{x}{a})\, k_1]\, 10^4$
0 507	60	25
0 619	80	26
0.732	120	27

4. These tables show that the immutability of the expression in the third column is satisfactory. In HENRI's experiments those values differ but little more than those of the invertin action. To some extent the experimental errors may certainly be attributed to the sensitiveness of the emulsin and partly also to the method followed. The table with TAMMANN's experiments proves this. The constants vary within rather large limits but agree reasonably with an average value.

5. If we now accept the hypothesis of the negative [2]) autocatalysis, and after what has been stated this seems to me quite permissible, there will be found to exist an evident parallelism between the action of emulsin [3]) and invertin.

The ferment-reactions which up to the present have been accurately studied proceed therefore according to the scheme:

$$\frac{dx}{dt} = (k_1 \pm k_2 x)(a-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which k_2 may also be zero [4]).

This, however, only means that k is constant for the same series of experiments or for a definite concentration of material [5]) and enzyme.

We may say that there exists a function of the form:

$$k_1 = F(a, b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which a is the concentration of the invertable matter and b that of the ferment.

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[1]) Compare TAMMANN, Zeitschr. für physikalische Chemie. 3, 27 (1889).

[2]) This may be one of the causes that the synthetical experiments with emulsin (TAMMANN, EMMERLING) have given a negative result

[3]) This is probably also the case with other ferment-reactions.

[4]) It is not inconceivable that cases may occur where if t is small, x would at first act positively and afterwards negatively.

[5]) Up to the present it is only haemase for which SENTER (Zeitschr. für physikalische Chemie **44**. p. 257, (1903)). has obtained different results within a small concentration limit.

In any case we may conclude that the differential equation (11) is incomplete and that it would be better to give it the form for a reaction of a higher order[1]).

$$\frac{dx}{dt} = (k_1 \pm k_2 x)(a-x)b \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which corresponds within certain limits with experience[2]).

Generally this relation is expressed by the equation:

$$\left(\frac{b_1}{b_2}\right)^n = \frac{k_1}{k_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

From TAMMANN's[2]) experiments with emulsin it appears that in any case

$$n = F(a, b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

It is also important to observe that k_1 is apparently only changeable within the limits of the experimental errors, whether we start from the concentration a_1 of the substances to be inverted or whether we choose as the starting point the concentration $a_2 + x$, in which $a_2 < a_1$ and x corresponds with an amount of inverted product corresponding with $a_1 - a_2$; HENRI has already pointed this out for invertin.

From $\frac{ak_2}{k_1}$ = constant we obtain the somewhat unexpected result:

$$\frac{a}{\alpha} = \frac{\frac{k_1}{k_2}}{\frac{\gamma_1}{\gamma_2}}$$

in which a and α represent the concentrations of the substances undergoing inversion, k_1 and k_2, γ_1 and γ_2 the corresponding velocity constants. I hope shortly to revert to this matter.

The matter communicated here has no connection with the later formulation of HENRI[4]) which I cannot yet accept as conclusive.

Utrecht, Lab. gen. and inorg. Chemistry University.

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[1]) The formula $\frac{dx}{dt} = (k_1 - k_2 x)(a - x) = k_2\left(\frac{k_1}{k_2} - x\right)(a - x)$ represents indeed an expression for a bimolecular reaction.

[2]) Compare, Zeitschr. für physiologische Chemie. **37**, 159. (1902).

There is an evident connection with HOFMEISTER's experiments (Zeitschr. für physikalische Chemie) **17**, 1 (1895) but it seems to me that we must not think with HÖBER (Physikalische Chemie der Zellen und Gewebe, 1902 p. 312), of any dissociation of the ferment, but rather of that of the substances dissolved therein. Like HÖBER however, I attach no particular importance to an explanation of this kind based on analogy.

[3]) Zeitschr. für physikalische Chemie. **18**. 426, (1895).

[4]) Lois générales. p. 107.