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**Physiology.** — "*Experimental researches on the analogy between swelling (imbibition) and mixing.*" By J. R. KATZ. (Communicated by Prof. C. A. PEKELHARING).

(Communicated in the meeting of November 26, 1910).

Among the chapters of General Physiological Chemistry there are few which invite to a further study so much as that on swelling. Partly, because so little is known and understood as yet, about this phenomenon already noticed in ancient times, and also because the knowledge of the laws of swelling and the explanation of the imbibition process prove to be of fundamental significance for physiology, pharmacodynamics and preparative physiological chemistry.

For physiology, because the protoplasm and the cellnucleus (which together form the material substratum which is the seat of life) are built up of a system of imbibing bodies and interposed liquids. Many phenomena of life are associated with the motion of water from those solid bodies to the surrounding liquids (or reversedly) and between those bodies mutually. And it has often been tried to attribute to those water displacements a fundamental significance by making them the basis of an explanation of those processes of life. So for instance, in the theory of the muscular contraction of ENGELMANN<sup>1)</sup>, who, guided by extended *morphological* researches as to the changes in the contracting muscle, has tried to demonstrate that the transformator by which the chemical energy of the metabolism in the muscle is converted into mechanical power, consists of a system of imbibing bodies and acts by displacement of water between these bodies mutually. "During the contraction the anisotropic layer swells owing to imbibition of water which it derives from the isotropic layers with which it comes into contact. Each anisotropic layer is, so far as the muscular fibre extends, provided at both sides with a layer from which it can draw water, which it can again return when the contraction ceases." <sup>2)</sup>

By means of this hypothesis many facts which are noticed in the contraction of the muscle are explained qualitatively, and ENGELMANN demonstrated by his well-known violin string pattern that the theory can also account, more or less, for the form of the line which

<sup>1)</sup> Summarized in his Croonian Lecture, Proc. Roy. Soc. vol 57, p. 411-433.

<sup>2)</sup> PEKELHARING (Voordrachten over Weefselleer, p 338) thus summarises ENGELMANN'S views.

represents how the length of a contracting muscle depends on the time. But this is not enough. The success with which WERTHEIM, SALOMONSON, HOORWEG and others have been able to represent the curves experimentally obtained by formulae relatively so simple, points to the fact that the theory, if really satisfactory, will have to lead to similar formulae. But in order to work out the theory so far, it is necessary, however to know the quantitative laws of swelling; to know on what it depends whether in a system of imbibing bodies the water will, or will not, be displaced, and according to what formulae the different properties of a swelling substance depend on the degree of imbibition.

*For pharmacodynamics.* A drug absorbed in the blood, when it has been administered in small doses, frequently affects the function of one organ only and this is explained by assuming that a substance causes *ceteris paribus* a more drastic change in the life processes of an organ when it is present in a greater concentration and by the fact that different organs absorb very different quantities of a drug from the same solution (blood for instance). This creates a connection between elective action and relative strength of the imbibition in different kinds of cells <sup>1)</sup>, which has proved fruitful as a working hypothesis. Of late years a commencement has been made to work out this theory also quantitatively. The elegant researches of W. STRAUB on the action of veratrine on the Aplysia heart and the immunochemical theories of ARRHENIUS may be cited as examples. In all these calculations it is assumed that the so-called division rule of NERNST (a sequel of VAN 'T HOFF's laws of dilute solutions) is also available for the imbibition of dissolved substances in swelling bodies. However interesting and plausible these applications may appear, it admits in my opinion of serious doubt whether in all these cases the laws of dilute solutions have been used within their proper limits. <sup>2)</sup> If they have not, the argument would, in some cases, not rest on a sufficiently firm basis, notwithstanding its apparent solidity.

This difficult question can only be answered when a thorough knowledge of quantitative laws and an explanation of the swelling process is obtained.

*For preparative physiological chemistry.* All polysaccharides and albuminous substances undergo swelling in water and it is greatly in consequence of this property that the chemistry of these substances

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<sup>1)</sup> Compare H. J. HAMRURGER, De physische scheikunde en hare betoekenis voor de geneeskundige wetenschappen, 1901, pag. 7, 20.

<sup>2)</sup> I will refer to this important question in detail, later.

is of such a peculiar character. The criticism of the methods for the purification of these substances, the characteristics of their purity, the question whether the water contained in imbibing crystals may be put — at least in part — on a par with the water of crystallisation of inorganic salts (as pretended by HOPPE SEYLER<sup>1)</sup> and others in the case of oxyhaemoglobin crystals), the question whether the molecular weight of the imbibing substances can be determined from the decrease of their water vapour pressure, and so many other questions of that kind, are problems which the physiological chemist has, so to speak, to face daily, but which cannot be treated fully before the quantitative laws of swelling, and a due explanation of the same shall have been discovered.

But relatively little being known of this matter at that time, I have been engaged since the summer of 1904 upon an extensive research in order to get a better insight into these quantitative laws and their explanation. Very soon, some remarkable regularities and analogies were brought to light. I thought it desirable, however, not to publish these results before they had been confirmed so repeatedly that they could not be looked upon as being merely accidental.

In October 1906 I had found the analogy now described in this first publication, and communicated the same to my teachers Profs. H. W. BAKHUIS ROOZEBOOM and A. SMITS. In this paper I will give only a brief and partial account of the experiments carried out. For experimental details and the literature on the subject the more extended publication which will appear shortly, should be consulted.

#### *Short description of the phenomena of swelling.*

Before describing the researches on imbibition it appears to me desirable to point out, briefly, which phenomenon I have studied, from which similar, but yet different, phenomena it must be distinguished, and in which substances it is met with. This seems to me particularly desirable because these facts are sometimes mentioned in physics and chemistry under another name.

By *swelling* or *imbibition power*<sup>2)</sup> the biologists understand the

<sup>1)</sup> Cf. SCHÄFFER's Textbook of Physiology, I. p. 205 (1893).

<sup>2)</sup> The majority of investigators understand by imbibition power the same as swelling power. REINKE (HANSTEIN's Botan. Abh. IV, p. 2 and 3) differs from this view; his idea of imbibition power includes porosity as well. I do not

property of some solid substances, which under the most powerful microscope do not show visible pores, to occlude liquids between their smallest particles. If they are examined again after the absorption of the liquid it is impossible to distinguish the separate particles of the liquid and the solid substance even when using the most powerful lenses.

During this absorption of liquid the smallest particles of the solid body are separated from each other by the penetrating molecules of water. REINKE has called this increase of the distance between the particles the *increase of disgregation* of the solid substance. Because those particles get at a greater distance from each other, the volume and length measurements of the solid body suffer an increase<sup>1)</sup>; hence the name "swelling". At the same time the cohesion between the particles of the solid substance appears to have much decreased<sup>2)</sup>.

On the other hand we may expect that there will exist a great affinity between the water and the solid body if this is able to overcome the so powerful cohesion of the solid substance. This suspicion is confirmed; during the swelling a considerable amount of heat is liberated<sup>3)</sup> and an important contraction of volume takes place, in other words, the volume of the swollen body is considerably smaller than the sum of the volume of the solid substance and that of the imbibed water.

On drying, the swollen bodies can again part with the liquid absorbed; if this takes place slowly the homogeneity is retained. The phenomenon is — at least in the main — reversible.

Some swelling bodies, such as casein, wood, etc. when placed in contact with saturated water vapour absorb only a limited quantity of water and a so-called maximum of imbibition is reached (bodies of limited imbibition power); others such as gum arabic and peptone take up an unlimited amount of water causing them to become more and more fluid so that they, finally, get converted into a liquid mixture of water and imbibing substance (bodies of unlimited imbibition power).

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agree with him. The above definition is borrowed from HUGO DE VRIES, *Leerboek der Pflanzenphysiologie*, 4e Ed, p. 149-150 and from H. A. LORENTZ, *Leerboek der Natuurkunde*, 2e Ed., Vol. I, p. 419.

<sup>1)</sup> Sometimes very considerably; peas double in size, Irish moss (*Chondrus crispus*) swells to treble its size. (HUGO DE VRIES, loc. cit. 4e Ed. p. 150).

<sup>2)</sup> REINKE (loc. cit. p. 31) found that if air-dry *Laminaria* absorbs 300 % of water its ductility increases sixty fold while the breaking strain falls to one-tenth of its value.

<sup>3)</sup> If *amylum tritici*, dried at 90°, is stirred with its own weight of water, the temperature rises more than 10° (NÄGELI, *Theorie der Gährung*, (1879 p. 133-134)

On no account must imbibition be confounded with the porosity of some solid substances such as bricks, gypsum, and others which by surface adsorption and capillarity can absorb liquids in *visible preformed pores*. NÄGELI<sup>1)</sup> in 1858 already pointed out the difference between these two properties. In the porous absorption of water, the particles of the solid body are not forcibly separated; there is no increase of disintegration, therefore no increase in size and no loss of cohesion. Typical imbibition is, therefore, sharply distinguished from typical porosity.

It is principally among the products derived from living organisms that the imbibition power is often, in fact almost regularly, met with. Not only nearly all such substances (cellular walls, fibres, flour, wood, whalebone, leather, horn, etc.) possess swelling power but the pure physiologico-chemical compounds derived therefrom appear to possess these properties also.

Yet, the imbibition power is not limited exclusively to substances of vital origin. It is also observed in synthetically prepared and in inorganic substances; as instances, I cite copper ferroryanide, clay, tricalcium phosphate, and silicic acid.

The solid substances capable of imbibing water<sup>2)</sup> are amorphous, crystalline, or organised. The majority is amorphous that is to say, possesses no visible regular arrangement of particles<sup>3)</sup>.

1) Die Stärkekörner, Zürich, F. SCHULTHEISS, 1858, p. 332, 343.

2) Substances are known which absorb liquids other than water; caoutchouc, for instance, imbibes ether, oil, pyridin, and even liquid carbon dioxide; nitro-cellulose swells in alcohol-ether mixtures and in nitroglycerol. It is possible that the imbibition laws in some of these organic liquids are more simple than in the case of water because this is partly associated to complex molecules (perhaps  $H_2O_2$ ) and because the association degree of the imbibed water must necessarily alter. For physiological purposes the behaviour with water is, for the moment, the most important matter and therefore, I will limit myself to this.

On the imbibition in aqueous solutions of salts, whereon HOFMEISTER, SPIRO, PAULI, WO OSTWALD, H. FISCHER among others have made interesting experiments, I will deal when I have dwelt on the imbibition power in pure water.

3) In practice it is sometimes difficult to decide whether an imbibing substance is amorphous or crystalline. For, the external form of a typical crystal, with its regular limitation by flat planes, may be wanting without the substance ceasing to be crystalline. On the other hand an amorphous swelling body may, owing to tensions on drying, exhibit optical phenomena which remind one strongly of those by a crystalline substance (compare the experiments of AMBRONN, Ber. der Sächs. Gesellsch. d. Wiss. 1891 p. 349). The mere presence of anisotropism is, therefore, not in the least sufficient to prove a substance to be crystalline. So long as crystallography does not throw more light on this obscure question, I think it best to look on imbibing substance as amorphous, unless there is sufficient evidence to call it crystalline or organised.

The existence of *swelling crystals* is in my opinion one of the most remarkable facts which have become known in the study of the imbibition phenomena. It is certainly very striking that a typical crystal with its characteristic optical phenomena and corresponding cleavage planes can imbibe water without loss of its crystal nature and its homogeneity. But it creates still more surprise to notice that *all* known crystals of polysaccharides or albuminous bodies undergo swelling in water. It does not seem easy to explain how a crystal can swell while preserving its crystal nature. But no theory of imbibition can be called satisfactory unless it can fully account for this fact. The swelling crystals appear to me the touchstone of the imbibition theories.

Next to the amorphous and the crystalline swelling bodies, organic nature yields quite a series of products such as starch granules, bark fibres, woody fibres etc. which possess no crystal form, but instead, an arrangement of particles with corresponding optical phenomena and cleavage planes <sup>1)</sup>. Some investigators have felt inclined to look upon these so-called organised bodies <sup>2)</sup> as crystals with atypic limitation planes; others as amorphous substances wherein tensions occur. Neither of these two ideas seems to me quite satisfactory. And, provisionally, I think the best thing is to look upon the organised matters as a separate group, being more or less a medium between the amorphous and crystalline substances <sup>3)</sup>.

*The analogy between swelling and mixing.*

The fact that a certain analogy exists between the processes of swelling and mixing had been already observed by BERTHOLET in 1803. In his "Essai de Statique Chimique" he explains both processes by the same mechanism <sup>1)</sup>. The physiologists who have worked in the third quarter of the nineteenth century on the subject of swelling — I only mention, CARL LUDWIG, NÄGELI, REINKE — also show in their publications in various places that they have noticed the existence of that analogy.

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<sup>1)</sup> Illustrations are given in each text-book of botany.

<sup>2)</sup> Amongst the organised bodies must also be reckoned the anisotropic layers of grained muscles.

<sup>3)</sup> Whether it is more in particular amongst the organised bodies that the much looked for continuity between amorphous and crystalline aggregation condition is perhaps to be found, is a question which I can only propound, but not answer. Cf. also the facts mentioned by W. PFEFFER, Pflanzenphysiologie I, p. 69—70.

<sup>4)</sup> Compare Vol. I, p. 34 and 38.

In order to get a clear idea of the analogy one should imagine a space containing water vapour in which are placed near each other a globular shaped imbibing substance (for instance a piece of sharply dried gelatin or gum arabic) and a drop of a liquid which is not readily volatile but easily mixes with water (for instance sulphuric acid or glycerin). Both now appear to be hygroscopic, both absorb water without loss of homogeneity; both *increase in size* because the volume of the mixture like that of the swollen substance is, approximately, additive and because the substance remains homogeneous during the water absorption. By this dilation without loss of homogeneity<sup>1)</sup> the particles of the swelling body, like those of the sulphuric acid, or glycerin get further removed from each other; in both the disgregation, as REINKER calls it, of these particles increases. If the two phenomena are compared more closely, it appears in both cases that the water absorption is accompanied by a considerable evolution of heat and a decided contraction of volume. There is only one point of difference between the two phenomena; the swelling body possesses the solid aggregation condition and retains the same during the absorption of the water whereas the miscible substance is liquid and remains liquid.

This gulf is, however, more or less bridged over by what is observed in the substances with unlimited imbibition power. If, for instance, powdered gum arabic is allowed to take up moisture, it begins to cake when 30 % of water has been absorbed, with 40 % it forms a plastic mass, with 60 % it is still solid but soft and when 110 % has been absorbed a watery solution of gum arabic is obtained which becomes less viscous on further dilution. Ovalbumin, peptone and dextrin behave in the same manner. Here we see how typical swelling substances *gradually* become aqueous mixtures, owing to water absorption. The two phenomena, therefore, not only resemble each other, but must be indeed closely related. Or perhaps even identical?

The older investigators have not dared to assent to the identity,

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<sup>1)</sup> One might perhaps object that the aqueous solution of gum arabic so formed is not a real but a colloidal solution. In the case of substances such as gum arabic, dextrin, and peptone, the difference between real and colloidal solution is but very slight. That this objection is not of great importance is shown by the fact that solutions of substances devoid of colloidal properties such as fructose (which has a low molecular weight and possesses normal values for the lowering of the freezing point and the elevation of the boiling point) are also gradually converted on drying (if crystallisation is prevented) into a solid substance having all the properties of a swelling substance. The sodium salt of glycerol-phosphoric acid behaves similarly.



although they noticed plainly the close relationship. REMKE, who in 1879 discussed <sup>1)</sup> the analogy and observed it more keenly than any one before him, evidently still hesitated — as in fact all his contemporaries would have done — to assume that *miscibility* should exist in the *solid* condition.

But the development of physical chemistry in the last twenty-five years has removed this difficulty. In 1890 VAN 'T HOFF published his celebrated theory of the solid solutions, which shows that miscibility exists in the solid condition just as well as in the liquid state, and the cases have become almost innumerable where this miscibility has been actually observed. In consequence, the difficulty of the older writers has been removed and now, I ask, what can still prevent us from assuming that swelling means mixing <sup>2)</sup>, in other words that *when a solid substance swells in water, this depends on the formation of a solid solution of water in the imbibing body* <sup>3)</sup>.

Of great significance to the problem of imbibition, seems to me to be TAMMANN's idea <sup>4)</sup> that amorphous solid substances are in many cases nothing but liquids of very great viscosity. TAMMANN showed that all possible liquids, if they are cooled rapidly enough to prevent crystallisation, become *gradually* more and more viscous and are converted, without any discontinuity, into solid amorphous bodies; known instances of this are glass, cane-sugar, glycerin. This view, also warmly defended by BAKHUIS ROOZEBOOM and O. LEHMANN, throws a remarkable light on the fact that the substances of unlimited imbibition power (which are all amorphous), when absorbing water, are converted continuously into aqueous solutions. It leads us to the hypothesis that *amorphous swelling bodies are substances of so great a viscosity that they practically possess the solid aggregation condition, but have still retained their miscibility with water*.

If this hypothesis is correct the swelling of a piece of gelatin and the water absorption of such liquids as sulphuric acid and glycerin

<sup>1)</sup> Loc. cit. p. 123—128.

<sup>2)</sup> The substances of limited imbibition power would then be analogous to those of limited miscibility, those of unlimited imbibition power to those of unlimited miscibility. Limited and unlimited miscibility are not different properties; in substances with a critical mixing point both pass into each other at a change of temperature.

<sup>3)</sup> Similar hypotheses have been propounded repeatedly by physico-chemists. But they have not worked out this supposition any further, to ascertain whether it can be used as a working hypothesis in the investigation of the quantitative laws of the imbibition power.

<sup>4)</sup> Compare Zeitschr. f. physikal. Chem., 25, p. 469—479.

will not only agree qualitatively but the *quantitative laws of the two phenomena will probably be the same.*

*Experimental research as to the analogy in the quantitative laws of the two phenomena.*

Whatever value one likes to attach to the theory of imbibition advanced, it leads in any case to a thesis which can be controlled experimentally.<sup>1)</sup> I have, therefore, instituted a comparative research as to the quantitative laws of imbibition in a number of amorphous swelling bodies and as to the miscibility in a number of comparable miscible substances; as such I have chosen three liquids, which like imbibing bodies are practically non-volatile and can like these absorb large quantities of water, namely sulphuric acid, glycerin and ortho-phosphoric acid.

In the case of a number of amorphous swelling substances, I determined, experimentally, the quantitative relations according to which the heat of imbibition, the water vapour pressure and the volume contraction depend on the degree of imbibition; the results obtained were represented graphically. In a few cases I could make use of measurements executed by other investigators.

Afterwards, I did the same with the three miscible liquids. For the greater part I could make use here of measurements already carried out by previous investigators for other purposes. But the water vapour pressures of glycerin- and phosphoric acid-mixtures had to be determined by myself and the heat generated on mixing glycerin and water was measured in a series of experiments carried out jointly by myself and Mr. J. J. P. VALERTON.

When choosing the swelling substances investigated, I have been careful to avoid unnecessary complications. For instance, such substances as amyllum in which layers rich in moisture occur alternately with layers poor in moisture do not seem to me suitable for the research; for each of these layers has a different imbibition power and the phenomenon observed is composed of the sum of numerous elementary phenomena which obey different laws. *A fortiori* intricate products such as peas or Laminaria in which all kinds of elements as cell walls, cell nuclei, starch granules etc. are adjacent to each other are quite out of the question. I have also avoided using sub-

<sup>1)</sup> Experiments of BÜTSCHLI, VAN BEMMELLEN among others suggest that in some swelling substances there may be complications, so that the water absorption is not only due to swelling, but partly to capillarity (in preformed pores). In such cases we might expect to find different quantitative laws.

stances such as freshly precipitated silicic acid, or metallic hydroxides wherein probably slow chemical changes take place. For instance the blue cupric hydroxide when in contact with water gradually changes to the black oxide — slowly at the temperature of the room, rapidly at the boiling heat; the brown ferric hydroxide turns red, stannic acid passes into metastannic acid and silicic acid requires an increasing amount of potassium hydroxide to redissolve. Fortunately in the case of albuminous substances and polysaccharides (of which the biologically important substances mostly consist) such complications do not seem to occur; spontaneous peptonisation, which might occur to the mind, does not proceed (at the temperature of the room, and whilst possessing a neutral reaction) with appreciable velocity. In those cases where I have extended my researches to metallic hydroxides etc. I have provisionally, confined myself to substances which by ageing artificially — prolonged heating under water — had been freed as far as possible from this complication. To make quite sure, the samples of the other substances tested were at least one year old.<sup>1)</sup>

*a. Heat of imbibition and heat of mixing.*

The quantity of heat ( $H$ ) was determined (in gram calories) generated when one gram of dried substance<sup>2)</sup> takes up  $i$  gram of water; this quantity I will call the imbibition heat at the imbibition degree  $i$ <sup>3)</sup>. The substance was put into a glass tube fitted with an india rubber stopper which was then placed in a calorimeter filled with water until there was an equilibrium of heat. By smashing the bottom of the

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<sup>1)</sup> All the substances were investigated in the powdered condition; check experiments had shown that the water adsorption at the surface of the grains of the powder was so small that no hindrance to speak of occurred.

<sup>2)</sup> The name "dry substance" is somewhat vague. I chose as such the substance dried at 110° in vacuo over sulphuric acid. In this manner all the different substances have been obtained as much as possible in a comparable condition.

The substances with the lowest water content with which I have carried out measurements were those dried over sulphuric acid at the temperature of the room; the values for the "dry" substance were obtained by extrapolation. In the case of a few substances which cannot be heated to 110° without decomposition I have determined the water by drying in vacuo over sulphuric acid at the temperature of the room; this is then mentioned separately. RODEWALD and his pupils KATTEIN and VOLBENN applied this method of water determination to all substances they investigated. The results of the two methods usually differ  $\frac{1}{2}$  to 1<sup>0</sup>/<sub>10</sub>.

<sup>3)</sup> The imbibition degree  $i$  therefore is the number of grams of water  $i$  absorbed by one gram of dry substance.

tube or by pouring over the content of it the substance was brought into contact with the water and the rise in temperature read off.

The form of the curve indicating how  $W$  depends on  $i$  has been determined with six substances, of which I only communicate those of *cellulose* (ash-free filters of SCHUMMER & SCHÜLL.) and *casein* (*pur.* HOECHSTER-FARBWERKE<sup>1)</sup>). Of the curves published by other investigators, only those of RODEWALD and KATTEIN for *artificially prepared starch granules*<sup>2)</sup> and of VOLBEHR for *prepared woody fibres*<sup>3)</sup> (as in the determination of crude fibre) seem to me fit for comparison with liquids. The other substances investigated by RODEWALD and KATTEIN were species of *amylum* which, owing to their stratiform structure, form more intricate objects; but there also curves were found which in form agree completely with those of artificial starch granules<sup>4)</sup>.

On the annexed illustration the curves of these four substances, carefully drawn to scale, are shown. All four make the impression of a hyperbola; this is particularly striking in the case of cellulose and casein<sup>5)</sup>.

In the case of the other two curves and the cellulose I have questioned whether they may, indeed, be represented by the formula of the hyperbola

$$W = \frac{Ai}{B + i}$$

The subjoined tables show that the agreement is satisfactory<sup>6)</sup>.

<sup>1)</sup> I beg to offer my sincere thanks to the directors of the Hoechst-Farbwerke vorm. MEISTER, LUCIUS and BRÜNING for kindly placing at my disposal the casein required for these experiments.

<sup>2)</sup> Zeitschr. f. physikal. Chem. **33**, p. 581.

<sup>3)</sup> Untersuchungen über die Quellung der Holzfaser, Inaugural-Dissertation, Kiel (1896) p. 32. VOLBEHR had also observed that the line determined by him had the character of a hyperbola.

<sup>4)</sup> *Amylum solubile* (MERCK) is, for reasons to be stated afterwards, not fit to be compared with liquids; for the rest it presents a line of the same form.

<sup>5)</sup> In the case of the other four substances which I have investigated, lines were also obtained which make the impression of hyperbolas.

<sup>6)</sup> The deviations are not much greater than the presumable experimental errors.

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HEAT OF IMBIBITION OF CELLULOSE. HEAT OF IMBIBITION OF ARTIFICIAL STARCH GRANULES.

A = 11.6 B = 0.030  $\Sigma \Delta^2 = 0.59$

dry = dried in vacuo over sulphuric acid at the temperature of the room.

A = 46.65 B = 0.148  $\Sigma \Delta^2 = 1.33$

<i>i</i>	<i>W</i> determin.	<i>W</i> calculated.	$\Delta$
0.—	0.—	0.—	
0.014	3.5	3.7	+ 0.2
0.041	6.9	6.7	— 0.2
0.054	7.6	7.5	— 0.1
0.074	9.0	8.3	— 0.7
0.264	10.5	10.4	— 0.1

<i>i</i>	<i>W</i> determin.	<i>W</i> calculated.	$\Delta$
0.—	0.—	0.—	0.0
0.0136	4.4	3.9	— 0.2
0.0236	6.8	6.4	— 0.4
0.0347	8.4	8.9	+ 0.5
0.0424	10.4	10.4	+ 0.0
0.0549	12.2	12.6	+ 0.4
0.0970	18.3	18.4	+ 0.1
0.1218	21.0	21.1	+ 0.1
0.1716	25.3	25.0	— 0.3
0.2403	29.5	28.9	— 0.6
0.3135	32.0	31.7	— 0.3
0.3811	32.8	33.2	+ 0.4

HEAT OF IMBIBITION OF WOODY FIBRES.  
(determination of crude fibre).

A = 23.62 B = 0.0895  $\Sigma \Delta^2 = 0.19$

<i>i</i>	<i>W</i> determin.	<i>W</i> calculated.	$\Delta$
0.—	0.—	0.—	
0.0370	6.7	6.9	+ 0.2
0.0697	10.5	10.3	— 0.2
0.0924	11.9	12.0	+ 0.1
0.1269	14.0	13.8	+ 0.2
0.1525	15.0	14.9	+ 0.1
0.1742	15.7	15.6	+ 0.1
0.1964	16.2	16.2	+ 0.0
0.2166	16.5	16.7	+ 0.2

On the same illustration are shown the curves of the heats of mixing for sulphuric acid, glycerin, and orthophosphoric acid (here again the heat of mixing  $W$  represents the number of gram calories generated when one gram of dry substance takes up  $i$  gram of water. They exhibit a strong resemblance to the curves of the heat of imbibition.

The two subjoined tables prove indeed that they may be represented by a hyperbola.

HEAT OF MIXING OF SULPHURIC ACID  
AND WATER.

(THOMSEN).

$$A = 182.10 \quad B = 0.3303 \quad \Sigma \Delta^2 = 1.00$$

$i$	$W$ determin.	$W$ calculated	$\Delta$
0.—	0.—	0.—	—
0.1837	65.04	65.07	+0.03
0.3674	96.02	95.88	-0.14
0.5511	113.55	113.86	+0.31
0.9185	133.65	133.93	+0.28
1.653	152.45	151.78	-0.67
3.490	165.74	166.34	+0.60

HEAT OF MIXING OF GLYCERIN  
AND WATER.

$$A = 16.40 \quad B = 0.81 \quad \Sigma \Delta^2 = 0.51.$$

$i$	$W$ determin.	$W$ calculated	$\Delta$
0.—	0.—	0.—	—
0.1800	3.3	3.0	-0.3
0.3508	5.1	5.0	-0.1
0.609	6.9	7.0	+0.1
1.234	9.8	9.9	+0.1
1.788	11.2	11.3	+0.0
3.061	13.0	13.0	+0.0
6.170	14.2	14.5	+0.3
9.252	14.9	15.1	+0.2
12.32	15.3	15.4	+0.1
25.35	16.4	15.9	-0.5

Indeed, THOMSON<sup>1)</sup> was able in 1883 satisfactorily to express his researches on sulphuric acid by means of this empirical formula<sup>2)</sup>; and VAN DER WAALS's theory of mixtures leads to the same law.<sup>3)</sup>

As will be noticed the analogy between the quantitative laws of swelling and miscibility is striking indeed.

<sup>1)</sup> Thermochemische Untersuchungen, Vol. III, p. 8.

<sup>2)</sup> E. BOSE. (Physikal. Zeitschr. 6, p. 548-553) also praises the beautiful results which enabled THOMSON to represent his measurements of the heat of mixing by the hyperbolic formula.

<sup>3)</sup> Continuität des gasförmigen und flüssigen Zustandes, Vol. II, p. 45; as a matter of fact this deduction is made for non-associating substances only.

b. *Water vapour pressure.*

In the case of forty swelling substances, I have determined the curve according to which the aqueous vapour pressure of the swollen body depends on the degree of imbibition. That pressure has been expressed as fraction ( $h$ ) of the maximum pressure of water vapour at the same temperature.<sup>1)</sup> Such a line which is characteristic for the manner in which the imbibition water is contained in a substance, I will call the *hygrometric line* of the swelling substance. The determinations were carried out according to a method which agrees in the main with the one employed by VAN BEMMELLEN<sup>2)</sup>.

Of eight of these substances, the lines, again drawn carefully to scale, are shown in the illustration.<sup>3)</sup> They are *casein*, *cellulose*, *gelatin* (the best commercial, after being thoroughly washed with water), *peptone* (amphopeptone prepared by Dr. G. GRÜBLER according to KÜHN<sup>4)</sup>), *gum arabic* (finest commercial, in powder), *serumalbumin* (Albumin aus Blut puriss. Merck, dialysed, filtered and then evaporated at the temperature of the room), *tricalcium phosphate* (calcium phosphoricum tribasicum siccum Merck) and *artificially aged silicic acid* (acumid silicium Merck, heated for half a year under water at 80° C.). The first three and the last two have a limited imbibition power, the fourth, fifth, and sixth an unlimited one; some of these substances belong to the albuminous bodies, others to the polysaccharides, others again to the inorganic compounds. Although substances of a very different nature have, therefore, been used, all lines appeared to possess the same form<sup>5)</sup>. With small degrees of imbibition the curve

<sup>1)</sup> This quotient alters but very little on the rise or fall of the temperature; it is, therefore, advantageous to express the vapour pressure in that manner.

<sup>2)</sup> The difference with VAN BEMMELLEN's method chiefly consisted in the fact that a same portion of the substance did not pass successively through the different equilibria but that different portions of a same substance, after the same preliminary treatment (maximum drying or drenching), came each simultaneously in equilibrium over another sulphuric acid solution. This considerably shortens the time of the experiments otherwise so tedious.

<sup>3)</sup> A double arrow  $\updownarrow$  on the curve indicates that the equilibrium was approached from two sides, a single arrow  $\uparrow$  or  $\downarrow$  that it was reached from one side only and from which one. Check experiments with numerous substances have shown that the form of the lines obtained is the same whether the one or the other method is followed and that the equilibria reached differ but little quantitatively.

<sup>4)</sup> Apart, of course, from this difference that the curve for  $h = 1$  terminates with substances of limited imbibition power in the imbibition maximum, whereas with those of unlimited imbibition power, it takes an asymptotic course. But for the rest the lines of these two groups exhibit no difference.

begins to turn its convex side downwards, gets at a greater  $i$  a point of inflection and then turns the concave side downwards, forming a more or less S-shaped line.

So great an agreement with compounds so different chemically is somewhat surprising <sup>2)</sup>.

Apparently different from this are some of the results obtained by VAN BEMMELLEN. When experimenting with silicic acid freshly precipitated from soluble glass by hydrochloric acid and with ferric hydroxide recently precipitated by alkali from ferric chloride he obtained lines much more complicated, with three points of inflection. If, however, we examine the curves which he obtained from *old* silicic acid <sup>3)</sup> and ferric hydroxide <sup>4)</sup> more closely, they appear to possess the same form as I have found.

In the case of mixtures both experiment and theory lead to the conclusion that the line which indicates how the aqueous vapour pressure depends on  $i$ , can have two types which gradually pass into each other. With some substances, for instance with propionic and acetic acids, the concave side is, from the commencement, turned downwards and the point of inflection has disappeared. Glycerin appears to lie exactly on the border line, the curve represented still just shows the point of inflection.

The swelling bodies have, therefore, lines which agree with those of the miscible substances of the first group and bear, indeed, a close resemblance to these.

This analogy goes still further: miscible substances of the first group have a strong heat of mixing and contraction of volume; in those of the second group these properties are mostly but feebly positive or even negative. In all the imbibing substances, as yet investigated, they are strongly positive.

The theory of the mixtures makes one suspect <sup>1)</sup> that the initial

<sup>2)</sup> Curves of the same form were obtained by TROUTON with flannel and cotton wool, by ORME MASSON and RICHARDS with cotton wool, by LÖWENSTEIN with cupric ferrocyanide, zinc ferrocyanide and silicic acid formed by the action of dilute acid on silicates at the temperature of the room. I myself, have examined more than thirty other swelling substances, among those being the majority of the known physiologico-chemical substances and a few other products such as tannins and soaps; the curves invariably exhibited the S-shaped character.

<sup>3)</sup> Zeitschr. f. Anorgan. Chem. 13, p. 354 (fig. 17).

<sup>4)</sup> Zeitschr. f. Anorgan. Chem. 20, p. 207. The line of the jelly which has been kept under water for seven years is meant.

<sup>1)</sup> This follows from the approximative formulæ for concentrated mixtures described by NERNST as the formulæ of the "ideal concentrated solutions" and also from the expression derived by VAN LAAR from VAN DER WAAL's theory of

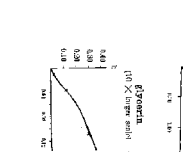
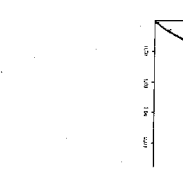
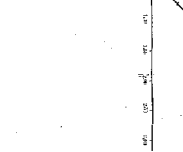
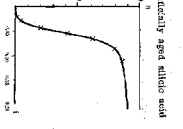
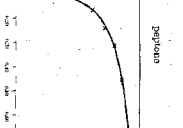
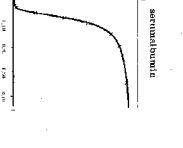
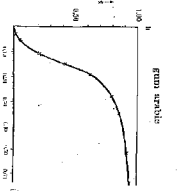
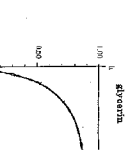
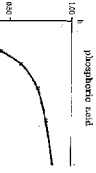
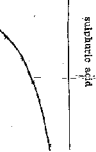
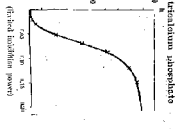
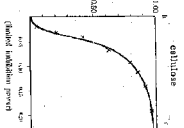
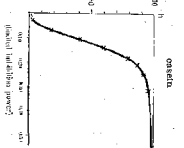
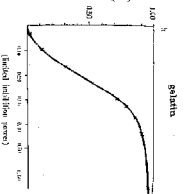
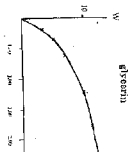
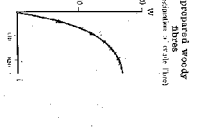
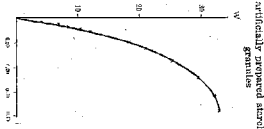
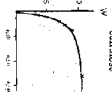
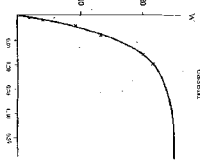


# IMBIBING SUBSTANCES.

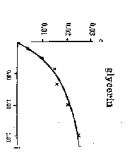
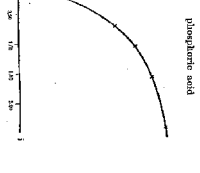
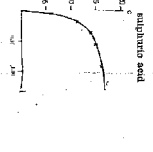
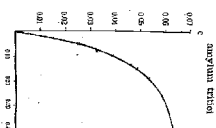
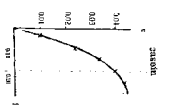
## a. heat of imbibition and heat of mixing.

# MISCIBLE SUBSTANCES.

## b. water vapour pressure.



## c. volume contraction.



turning downwards of the convex side (and the point of inflection caused thereby) will be the more pronounced in a miscible substance of the group when the so-called "differential heat of imbibition for  $i=0$ " is larger, that is to say, the quantity of heat generated when a large quantity of dried substance absorbs one gram of water<sup>2)</sup>. With sulphuric acid this character of the vapour pressure line is more strongly pronounced than with phosphoric acid, and with this substance considerably stronger than with glycerin. As will be noticed from the curve, the behaviour of the imbibing bodies lies more or less between that of sulphuric and phosphoric acid. We may, therefore expect as probable that the said heat quantity is greater in sulphuric than in phosphoric acid and much larger than in glycerin, and that in swelling bodies its values lie between those of the substances mentioned first. That such is indeed the case is shown by the subjoined table for the value of this quantity which I have calculated for the different substances from the caloric experiments.

casein . . . . .	200 cal.	sulphuric acid . .	550 cal.
cellulose . . . . .	390 „	orthophosphoric acid	100 „
artificial starch granules . .	320 „	glycerin . . . . .	20 „
woody fibres (estimation of			
crude fibre) . . . . .	260 „		
nuclein (from yeast) . . . .	200 „		

In the aqueous vapour pressure we find therefore also a resemblance, to in many details, between the quantitative laws of swelling and mixing.

*c. Volume contraction.*

In the case of three amorphous imbibing substances I have determined to volume contraction  $v$  (in cc) which takes place when one gram of dry substance absorbs  $i$  grams of water. The method was

mixtures, for the vapour pressure of mixtures. Particularly in the case of the dilatable substances the formulæ of NERNST seem to me to become of great significance. They predict for instance, that if the heat of imbibition is represented by a hyperbola, the hygrometric line must have the S-form, and various particulars of this line which are actually observed. I will refer to this more fully shortly in an article on the Thermodynamics of the Swelling Process.

<sup>2)</sup> The differential heat of mixing is calculated from the ordinary heat of mixing according to the formula  $w = \frac{dW}{di}$

quite the same as that described by RODEWALD for *amylum tritici*<sup>1)</sup>. Petroleumether (b. p. 80°—100° C.) was used as pyknometer-liquid which, as proved by check experiments, is not imbibed by the substances employed. Of the lines determined only those for casein are given; with the other substances I obtained lines of the same shape. I also had reproduced on the illustration the results of RODEWALD with *amylum tritici*, although these experiments are not of great worth for the purpose of comparison with liquids, owing to the presence of layers in the starch granules (in *amylum tritici*, however, this alternate construction shows but faintly). In both cases the curve exhibits the form of an hyperbola.

In the three miscible substances were found volume contraction lines of the same form<sup>2)</sup>; these curves also make the impression of being hyperbolas<sup>3)</sup>. In the volume contraction we also find, therefore, the same analogy in the quantitative laws of the two phenomena.

*d. Connection between heat of imbibition and contraction of volume.*

If the volume contraction  $c$  of a swelling substance is divided by the heat of imbibition ( $W$ ) at the same degree of imbibition, figures are obtained which, in the different imbibing bodies, are in the same order of magnitude. As this relation often changes considerably with the degree of imbibition, I calculated -- in order to obtain comparable values -- the quotient  $\frac{c}{W}$  for very small  $i$ 's ( $i = 0$ ).

In the three miscible liquids this quotient has also values which agree very well.

What is now particularly striking is that this order of magnitude is the same with miscible and with swelling substances. The subjoined table gives the value of  $\left(\frac{c}{W}\right)_{i=0}$ :

casein . . . . .	0.0015	sulphuric acid . .	0.0020
amylum tritici . . . . .	0.0019	orthophosph. acid.	0.0010
woody fibres (crude fibre determ.)	0.0021	glycerin . . . .	0.0024

<sup>1)</sup> Zeitschr. f. physical. Chem. 24, 201—202.

<sup>2)</sup> Calculated from experiments of DOMKE for sulphuric acid (LANDOLT, BÖRNSTEIN, MEYERHOFFER's Tabellen 3e Ed., pg. 328), of SCHIFF for phosphoric acid (Lieb. Ann. 37, pg. 192); of LENZ for glycerin (LUNGE's Techn. Unters. Meth. III, pg. 160).

<sup>3)</sup> THOMSON had pointed already out in 1883, that the volume contractions of acetic acid by mixing with water follow a hyperbola.

In swelling, as well as in miscible substances, the quotient, therefore, always lies between 10 and  $25 \times 10^{-4}$ ; however different the chemical nature of the substance may be! If the two phenomena are identical in nature, this need not cause astonishment. But how could this agreement in order of magnitude in such greatly different substances be explained if the two phenomena were different in principle?

*Summarizing*, we see that the laws of imbibition are relatively simple (much simpler than one would have expected after VAN BEMMELLEN's experiments) if only care is taken to avoid substances with secondary complications. And it appears that in the four cases where the quantitative laws of the imbibition power of amorphous solid substances were compared with the laws of the miscibility of liquids, a striking analogy exists. *The correctness of the fact that this analogy exists is independent of the correctness of the theory, which has led to the research.* But once found it is a fact with which every theory of swelling will have to reckon.

But whereas it forms a strong confirmation of the theory which proclaims that swelling is in principle the same as mixing, it will be difficult to propose any other theory which can explain unconstrainedly the existence of this analogy.

In a subsequent paper I hope to publish a number of experiments showing that the theory can also account satisfactorily for the imbibition power of swelling crystals.

**Physiology.** — "*Experimental researches on the analogy between swelling (imbibition) and mixing. 2<sup>nd</sup> Communication: Swelling (imbibing) crystals and mixed crystals*". By J. R. KATZ. (Communicated by Prof. PEKELIARING).

(Communicated in the Meeting of December 24, 1910).

*Experiments with swelling (imbibing) crystals.*

The question as to how the water of imbibition exists in swelling crystals<sup>1)</sup>, has for a long time excited great interest, but a clear insight is not yet obtained. In order that some more light may be thrown on this question it appeared supremely necessary to carry out new

<sup>1)</sup> Literature reviews on imbibing crystals are found in:

O. LEIMANN, *Molekularphysik* II, p. 550—553 (1888).

L. MAILLARD, *Revue Générale des Sciences* 9, p. 608—614 (1898).

FR. N. SCHULZ, *Die Krystallisation von Eiweisstoffen*, Jena, GUSTAV FISCHER.