The anhydride formed can be obtained by distillation, sodium pyrosulphate being left behind in the first case and sodium sulphate in the second case. The so obtained sodium pyrosulphate is very voluminous and on distillation with acetic acid and sodium acetate it again produces acetic anhydride. In this case refrigeration is not necessary when adding together the three components. If, however, the above pyrosulphate is first submitted to fusion a considerable decrease in volume takes place and it is then no longer capable of forming acetic anhydride, resembling in this respect a pyrosulphate prepared in the usual manner.

In the action of sodium chloride on acetylsulphuric acid acetyl chloride is formed. In a manner analogous to that of the preparation of acetylsulphuric acid from acetic acid and SO_3, were prepared butyrylsulphuric acid and benzoylsulphuric acid, from which were obtained in a corresponding manner butyric- and benzoic anhydride, respectively.

Chemistry. — *"Connexion between the adsorption-isotherm and the laws of* Proust *and* Henry.*"* By Dr. W. P. A. Jonker. (Communicated by Prof. Schreinemakers).

(Communicated in the meeting of February 28, 1914).

1. The adsorption-isotherm is of great importance for the study of the colloids. From various sides efforts have been made to find a connexion between this law and other laws of physical chemistry. Starting from the phase rule and the law of mass action which both can be deduced from the two main laws of thermodynamics, I have tried, in the subjoined lines, to trace the connexion between the adsorption-isotherm, the division rule and the law of constant proportions.

The question whether the phase rule may be applied unreservedly to dispersive systems will not be discussed here.

2. Let us imagine three substances A, B, and C. A and C form two non-mixable phases. C we may call the solvent (dispersive medium). B is soluble in C and can give a "compound" with A. (What kind of compound this is does not matter; it may be a chemical compound or an adsorption compound, or an ordinary solution).

When the equilibrium has set in we have $F = n + 2 - r$; when $n = 3$, $r = 2$ and p and T are constant, $F = 1$, therefore, the system is monovariant $(p$-$T)$. Which variables can occur here?

A and C form two phases between which B can distribute itself.

Therefore, we are dealing with the concentrations of B in the two phases. If we call the concentration of B in the dispersive medium: c and that in the phase $A \cdot \frac{x}{m}$ (in agreement with the notation used by FREUNDLICH in his "Kapillarchemie") it follows that in the monovariant $(p\text{-}T)$-system $\frac{x}{m}$ must then be $= f(c)$.

3. Only in the case where B in A yields a compound occurring in a separate phase, the system becomes non-variant $(p\text{-}T)$, hence

$$\frac{x}{m} = a \ (constant)$$

so that the "compound" is independent of the concentration.

We then speak of a real chemical compound that conforms to the "law of PROUST". This is in harmony with the idea of WALD, who for years has been trying to demonstrate that the constant composition, with which we credit our chemical compounds, is caused by the manner in which we generate these compounds. For we always utilise the occurrence of new phases (distillation, crystallisation, sublimation).

4. As a rule, however, $\frac{x}{m}$ will be a function of c.

The nature of this function may be determined by means of the law of mass action.

We now apply the same to the "compound" which B can form with A and call the number of gram. mols. of A, B and the compound m, p and q, respectively.

Let the formula of the compound be $A_{\frac{m}{q}} B_{\frac{p}{q}}$, then if

$$mA + pB \rightleftarrows q\, A_{\frac{m}{q}} B_{\frac{p}{q}}$$
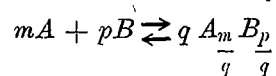
we get, according to the law of mass action,

$$\frac{C_A^m \, C_B^p}{C_{AB}^q} = k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this only the concentrations in which B appears are changeable.

If again we call $C_{AB} : \frac{x}{m}$ and $C_B : c$ then (1) passes into

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$$\frac{cp}{\left(\dfrac{x}{m}\right)^q} = k' \quad \text{or} \quad \frac{x}{m} = ac^{\frac{p}{q}},$$

in which a is constant. If, further, we put $\dfrac{p}{q} = \dfrac{1}{n}$ the well known adsorption isotherm

$$\frac{x}{m} = ac^{\frac{1}{n}}.$$

is formed.

5. This isotherm is generally a parabolic curved line that runs through the origin and the point $(1a)$. From the value

$$\frac{d^2\left(\dfrac{x}{m}\right)}{dc^2} = a\frac{1}{n}\cdot\left(\frac{1}{n}-1\right)c^{\frac{1}{n}-2}$$

we notice that the isotherm will turn the convex side towards the c-axis, when $\dfrac{1}{n} - 1 > 0$, and the concave side when $\dfrac{1}{n} - 1 < 0$.

The transition case lies at $\dfrac{1}{n} - 1 = 0$.

In the subjoined figure the course of the curve has been drawn for different values of $\dfrac{1}{n}$.
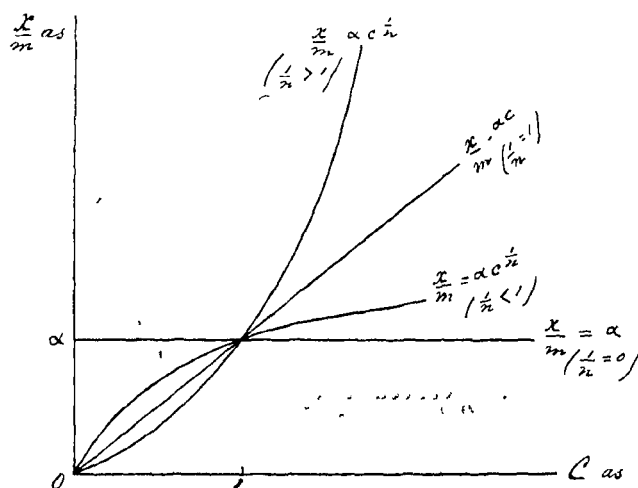
6. For $\dfrac{1}{n} = 0$, the isotherm passes into $\dfrac{x}{m} = a$, hence into a straight line parallel to the C-axis. This compound is, therefore, independent of the concentration and· consequently a "true chemical compound" obeying the law of PROUST (3).

7. If $\dfrac{1}{n} = 1$, $\dfrac{x}{m} = ac$ becomes a straight line through the origin, which cuts the line $\dfrac{x}{m} = a$ in the point (1. a).

The quantity of the substance B that passes into the phase A is then proportional to the' amount ·of the substance B in the solvent C, in other words, the law of division (HENRY's law applied to two liquid phases) is complied with.

In this case, in $\dfrac{x}{m} = ac^{\frac{p}{q}}$ (4) p must be $= q$, so that the equation of equilibrium now passes into :

$$m\,A + q\,B \rightleftarrows q\,A_{\frac{m}{q}}\,B,$$
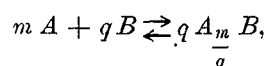
that is to say the substance B has the same number of atoms in the solvent C and in the phase A. This is also assumed in the law of division.

Some investigators are accustomed to speak of a "solid solution" in case the phase A is amorphous-solid. This denomination is likely to lead to confusion with mixed crystals so that, in my opinion, it would be better to use the expression "solution" if one does not like to introduce the word "pseudo-solid".

8. If $\dfrac{1}{n} > 1$ the convex side of the curve is turned towards the C-axis. We obtain such a line when, for instance, we draw the distribution of acetic acid in water and toluene. In such a case we never speak of "adsorption", but attribute the deviation from HENRY's law to "association".

In fact, from the equation of equilibrium

$$m\,A + p\,B \rightleftarrows q\,A_{\frac{m}{q}}\,B_{\frac{p}{q}}$$
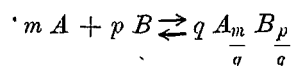
it appears that the substance B passes into the other phase as $B_{\frac{p}{q}}$, and $\dfrac{p}{q}$ being > 1, the number of atoms has increased.

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If $\dfrac{1}{n} < 1$ we obtain those cases which we are accustomed to call "adsorption". Analogous to (8) we ought to attribute here the deviation from HENRY's law to "dissociation". But nothing of the kind has been found experimentally.

10. Hence, in the above-mentioned matter, I believe I have demonstrated that HENRY's law (law of division) and the law of PROUST are special instances of the adsorption-isotherm. This is in complete harmony with the results of the investigations recently published by REINDERS [1] and GEORGIEVICS [2].

Zwolle, February 1914.

Mathematics. — *"Cubic involutions in the plane".* By Prof. JAN DE VRIES.

(Communicated in the meeting of February 28, 1914.)

1. The points of a plane form a *cubic involution* (triple involution) if they are to be arranged in groups of three in such a way, that, with the exception of a finite number of points, each point belongs to *one* group only. Suchlike involutions are for instance determined by linear congruences of twisted cubics. The best known is produced by the intersection of the congruence of the twisted cubics, which may be laid through five fixed points; it consists of ∞^2 polar triangles of a definite conic (REYE, *Die Geometrie der Lage,* 3e *Auflage,* 2e *Abtheilung,* p. 225). According to CAPORALI [3] it may also be determined by the common polar triangles of a conic and a cubic. A quite independent treatment of this involution was given by Dr W. VAN DER WOUDE [4].

In what follows only cubic involutions will be considered possessing the property that an arbitrary line contains one pair only, and is consequently the side of a single triangle of the involution. The

[1] Kolloïd. Zeitschr. 13 96 (1913).

[2] Zeitschr. f physik. Chem. 84 353 (1913).

[3] *Teoremi sulle curve del terzo ordine* (Transunti R. A. dei Lincei, ser. 3a, vol. 1 (1877) or Memorie di geometria, Napoli 1888, p. 49). If $a^3_x = 0$ and $b^2_x = 0$ are those curves, then the involution is determined by $a_x a_y a_z = 0, b_x b_y = 0, b_y b_z = 0, b_z b_x = 0.$

[4] *The cubic involution of the first rank in the plane.* (These Proceedings volume XII, p. 751—759).