

Citation:

H.R. Kruyt, Pseudoternary systems of acid anhydrides and water I. Phthalic anhydride, in: KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 712-718

Chemistry. — “*Pseudoternary systems of acid anhydrides and water. I. Phthalic anhydride.*” By Dr. H. R. KRUYT. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of December 27, 1913).

For reasons, which will be further explained in a following treatise of this series, the knowledge of the heterogeneous equilibria in systems of acid anhydrides and water seemed to me of importance. The only quantitative investigation that has been made on this subject is found in the dissertation of E. VAN DE STADT¹⁾ and relates to phthalic- and succinic anhydride. The results thereof may be summarised as follows: If we shake the acid with water at a definite temperature we soon attain an equilibrium; if, however, we shake the anhydride with water, we notice a continuous rise of the total-solubility²⁾ at which values are attained far above the solubility of the acid; then follows a period of fall quite as regular as the previous rise, no discontinuity occurs in this process; finally we again arrive, at the solubility of the acid. These results suggest the following interpretation: the anhydride has a greater solubility than the acid, hence occurs the provisional high total concentration, but

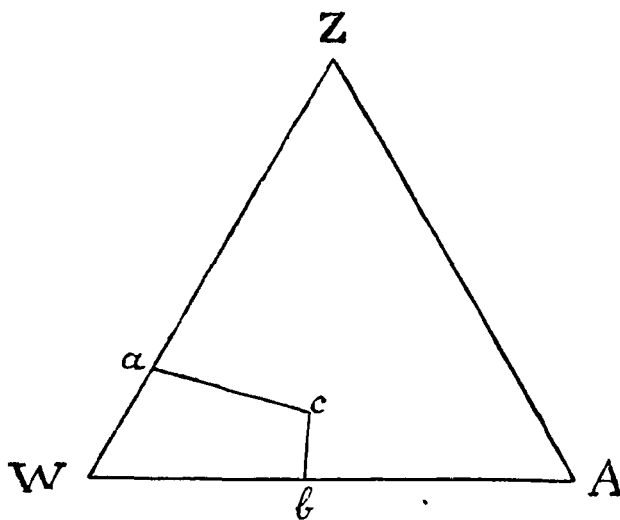


Fig. 1.

¹⁾ Amsterdam 1901. Also *Zeitschr. f. physik. Chem.* **31**, 250 (1899) and **41**, 353 (1902).

²⁾ By this is meant the acid concentration as found by titration which represents the sum of the acid- and anhydride molecules.

gradually the anhydride disappears by conversion into the acid and so we again finish with the acid-solubility.

This explanation, however cannot be satisfactory, for it is assumed herein that the phase equilibria set in while the reaction equilibrium is modifying the condition in the homogeneous solution. Thus we have a pseudoternary system: water-anhydride-acid (W-A-Z). In fig. 1 has been drawn the solubility-isotherm, the equilibrium line will about coincide with the axis WZ . The position of a and b is given by the assumed difference in solubility between the acid and the anhydride. If now we shake water and anhydride the solution will about follow the lines Wb and bc ; in c the solubility of the phthalic acid has been attained and if then a fall occurs in the total solubility this means to say that *solid phthalic acid* has deposited. But then the equilibrium is non-variant (p, t) and hence a fall cannot take place immediately after a rise; no continuous maximum can follow, but a long stop at the highest concentration must occur. Now this was not observed by VAN DE STADT; on repeating the experiment at 20° I also noticed that the concentration of a solution when shaken with phthalic anhydride in a rotating flask did not come to a standstill, but passed continuously through a maximum value.

In Table I this frequently repeated experiment is indicated. $N/10$ sodium hydroxide was used for the titration with phenolphthalein as indicator.

TABLE I.		
3.17 gr. Phtalicanhydride + 90 cc. water.		
No.	Time	Concentration in millimols per L.
1	$\frac{1}{4}$ hour	17.5
2	$\frac{1}{2}$ >	34.4
3	$\frac{3}{4}$ >	55.1
4	$1\frac{1}{4}$ >	46.2
5	$1\frac{1}{2}$ "	41.3
6	4 >	36.4

The solubility of phthalic acid is 35.2 millimols p. litre; it was always attained the next day.

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It should be noticed that in the interval between experiments 3 and 4 a finely divided solid mass had deposited (which very much impedes the filtration through cotton wool); indeed the experiments following have really been carried out with the two solid phases, anhydride and acid; even after experiment 6 a few long needles of anhydride were still readily visible.

Afterwards the shaking bottle was provided with acid as well as with anhydride so as to determine the position of point *c*. Now indeed a composition was attained that remained fairly constant for a longer time (see the first two columns of table II). But it seems peculiar that 1. the value found lies but little above the solubility of the phthalic acid and 2. that the value was found to differ in different experimental series. In the dissertation of VAN DE STADT we also find in the second table on page 49 an extremely smooth maximum as the progress of the solubility in the presence of the two solid phases.

Perhaps an explanation may be found here owing to a peculiar relation between the velocities of attainment of the homogeneous and heterogeneous equilibria. As this necessitates the knowledge of the proportion of anhydride to acid in the various solutions this proportion was determined. The chemical method applied by LUMIÈRE and BARBIER¹⁾ in the study of the equilibrium in the homogeneous system acetic-anhydride-water proved impracticable here, but the electric conductivity power previously applied by VOERMAN²⁾ and by RIVETT and SIDGWICK³⁾ in the study of the progressive change of the reaction in homogeneous systems, seemed to furnish a better method.⁴⁾

In order to render unnecessary the repeated withdrawal of large volumes of liquid a small plunging electrode was constructed with a capacity that just required suitable resistances for liquids used in these experiments.

We made use of DE HAËN's phthalic anhydride (m.p. 130°.6 in VAN EIJK's apparatus); phthalic acid was prepared from that anhydride by complete hydratation; titre and conductivity power of the saturated solution appeared to be independent of the quantity of solid phase, hence foreign substances were absent. By numerous determinations with concordant results we found for the solution saturated with phthalic acid:

¹⁾ Bull. Soc. Chem. de France [3] **33**, 783 (1905).

²⁾ Diss. Groningen 1903, Rec. d. Trav. Chim. d. Pays-Bas, **23**, 265 (1904).

³⁾ Journ. Chem. Soc. **97**, 732 and 1677 (1910).

⁴⁾ The method also has been applied by BOESEKEN and his collaborators, cf. Rec. d. Trav. Chim. d. Pays Bas 1912 and these Proceedings. (Note added in the English translation).

35.2 millimol. p. litre spec. cond. power **0.001952**.

If we take μ_{∞} for 20° on 0.333, OSTWALD'S law of dilution then yields $k = 0.117$, which result was put to the test in a number of solutions. The acid concentration may now be calculated from the specific conductivity power¹⁾.

The experiments were carried out by rotating a small flask in the usual manner in a thermostat. The conductivity vessel was furnished with a trebly perforated stopper. Through the stopper was put the plunging electrode, also a little tube leading to the cotton-wool filter and another one to which suction could be applied. Immediately after 11 cc. of the liquid had been withdrawn the resistance was measured in the usual manner (WHEATSTONE bridge, alternating current and telephone); 10 cc. were then pipetted off and titrated.

In Table 2 is found the complete composition of the solutions which are shaken with the two solid phases. We notice that although a totally stationary maximum value was not found, it is very surprising to find how remarkably little anhydride is contained in the solutions which during about two hours still change but little in composition.

Time	Titration	Spec. cond. power	Acid	Anhydride	Maximum average
11 min.	40.0	0.001970	35.8	4.2	} 37.0 acid 4.4 anhydride
27 >	42.1	2027	37.7	4.4	
65 >	41.1	2002	36.8	4.3	
96 >	41.5	2002	36.8	4.7	
147 >	40.7	1995	36.6	4.1	

Hence a large solubility of the anhydride molecules appears but little probable. It is interesting to notice that these solutions contain more phthalic acid than the purely aqueous ones. The solubility of the acid is thus much promoted by the anhydride present.

Fig. 2 appears to be the most appropriate one for expressing these results.

¹⁾ As to the neglecting of the influence of the anhydride on the conductivity power see RIVETT and SIDGWICK (l.c.).

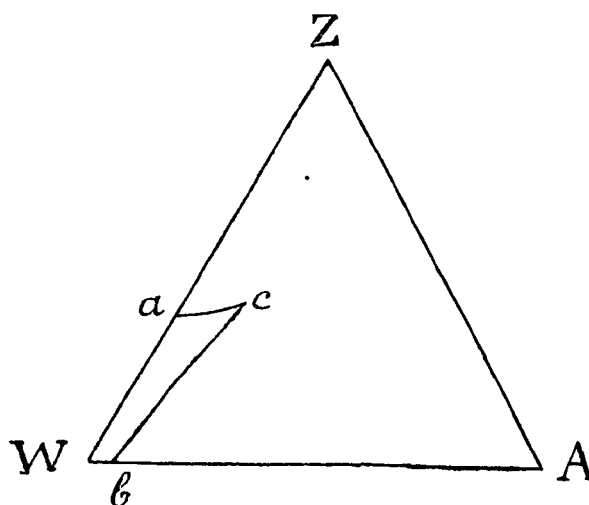


Fig. 2-

a lies at a greater concentration than b , the solution c contains more acid than a . Looking at the presumably very slight solubility of the anhydride and the fairly large reaction velocity of the hydration (four times greater¹⁾ than that of acetic and succinic anhydride) it will be understood why in different experimental series were found maximum values which mutually slightly differed. (Some tritration values from different series: 41,4 — 41,4, 44,0 — 44,3 — 44,5). Three processes are taking place continuously: solution of anhydride, hydration thereof and crystallisation of phthalic acid. The latter will no doubt take place spontaneously as a large quantity of finely divided solid phase is present: the second takes place fairly rapidly and the first is evidently not rapid enough to maintain the condition of the point c . That appears from table 3 where this last reaction

TABLE III				
2.25 gr. acid + 4.37 gr. finely powdered anhydride + 90 cc. water.				
Time	Titration	Spec. cond. Power	Acid	Anhydride
30 min.	43.7	0.002050	38.5	5.2
60 "	44.5	2056	38.7	5.8
101 "	44.1	2056	38.7	5.4
134 "	42.7	2027	37.7	5.0
222 "	40.8	1986	36.3	4.5

¹⁾ RIVETT and SIDGWICK l.c.

was promoted by adding a large quantity of finely powdered anhydride.

If we compare these results with those of Table 2, we notice that now indeed the anhydride-concentration has risen: as the acid concentration also lies higher this is evidently also promoted by the concentration increase of the other pseudo-component.

It now still remained to be seen whether the internal composition of the liquids which are shaken with anhydride only, agrees with the conclusions drawn from the above experiments.

In Table IV is shown the result of a measurement.

TABLE IV.				
3.11 gr. anhydride + 90 cc. water.				
Time	Titration	Spec. cond. Power	Acid	Anhydride
25 min.	29.2	0.001663	26.3	2.9
50 >	54.5	2286	47.0	7.5
75 >	47.2	2193	43.6	3.6

From this we notice that the large total-solubility found when shaking with anhydride is mainly an acid-solubility. In another series, for instance, 43.6 acid: 7.7 anhydride was found for the composition at the greatest total solubility. More than the sixth part can therefore never be put to the account of the anhydride. As originally no solid phthalic acid is present as a solid phase we are presumably dealing here with supersaturated solutions, although on the other hand, anhydride and acid seem to promote each others solubility. It is therefore, intelligible that, after the maximum has been attained we can plainly observe the separation of the phthalic acid in the liquid and also that the liquidum phase gets impoverished both in acid and anhydride. As regards the acid this is presumably the case in a much higher degree than indicated in Table 4 as the withdrawal, after the maximum concentration has been passed, always takes a few minutes on account of the clogging of the filter by the deposited exceedingly finely divided phthalic acid. In the meanwhile of course, a little of the anhydride from the clear liquid in the conductivity vessel becomes hydrated again before the measurement could be executed and thus a somewhat too high acid and a somewhat too low anhydride concentration is found.

The progressive change of the solubility is also characterised by the fact that after about 25 minutes, when the solubility of phthalic acid (35.2 millimol. per litre) has not yet been attained, the condition is already such that the solution contains a preponderance of acid. The idea that phthalic anhydride should be readily soluble is, therefore, without any foundation; the anhydride concentration can, moreover, not be calculated by simply deducting the solubility of the acid in water from the total solubility.

This last experimental series therefore also confirms our contention: the anhydride passes into solution as such and then becomes hydrated and this so rapidly in comparison with its solubility velocity that the non-variant (p,t) equilibrium is not attained, or at least not permanently so. The anhydride, if we will not credit it with an *abnormally* small solubility velocity (for which there exists no reason, just the contrary), has a much smaller solubility than the acid.

No measurements have as yet been carried out with succinic anhydride, but looking at the parallel behaviour of the two acid anhydrides similar relations may be expected there also.

Owing to the peculiar relations between the homogeneous and the heterogeneous reaction velocities in this kind of systems, we are here at the limitation where we may still speak of actual pseudo ternary systems. In connection therewith and other correlated questions the investigation of different systems is being continued.

Utrecht, Dec. 1913.

VAN 'T HOFF-Laboratory.

Chemistry. — “*The mechanism of the acid formation of aliphatic acid anhydrides in an excess of water*”. By Prof. J. BÖESEKEN and P. E. VERKADE. (Communicated by Prof. HOLLEMAN).

(Communicated in the meeting of December 27, 1913).

The communication of WILSDON and SIDGWICK¹⁾ on the hydration of some acid anhydrides induces us to give a short résumé of the results obtained by us when investigating the hydration of the aliphatic acid anhydrides.

This investigation²⁾ has already been announced by one of us some time ago. He had found that the hydration constant of the cyclic acid anhydrides was connected with the dissociation constant of the acids formed thereof. As it was his intention to get to know

¹⁾ Soc. 103, 1959 (1913).

²⁾ Recueil 31, 90 (1912).