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Purification Process by Solution Zone Passages

Part 2 *Process Practice*

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Two types of apparatus for the purification of inorganic salts by the travelling-heater zone-refining process, using water as solvent, are described viz. the closed tube system and the open tube system.

Impurity distributions after several zone passages have been determined experimentally, and compared with theoretically deduced distributions, for the purification of:
(*a*) Nickel ammonium sulphate doped with iron (II) ammonium sulphate, a system where the solute and impurity form a solid solution.
(*b*) Potassium di-hydrogen phosphate doped with potassium chloride, a system in which solute and impurity form a eutectic.

The application of the process to the purification of technical grade di-sodium hydrogen phosphate, copper sulphate and ammonium alum to give reagent grade material is also described.

1. Introduction

The principle of the travelling-heater zone-refining process (THZR) has been described and the impurity distribution along the crystallisate has been derived and analysed theoretically in the first [1] of this pair of papers. In this part the apparatus used for the process is described and the experimental results for some representative systems are presented and compared with theory.

2. Description of the Apparatus

Two types of apparatus have been constructed for the purification of inorganic salts using water as a solvent. With the first type, referred to as the closed tube system, the solute to be purified fills the entire tube section, while in the second type, the open tube system, it does not.

2.1. The Closed Tube System

The solute A is contained in a glass tube B, 6 cm in diameter and 220 cm long as shown in fig. 1. The solute is tightly enclosed in the tube by means of two bungs, C, made from three rubber discs fixed on a stainless steel bush. The bush allows movement of the bung in the tube by means of a drilled metal rod that can be screwed up in it allowing air through it.

The tube is supported at its extremities by the installation table, at the left-hand end by two rubber rollers and at the right-hand end by two cogs engaging on a cog, D, fixed to the tube. One of the supporting cog wheels is driven by an electric motor, enabling the tube to be rotated about its axis, thus stirring up the solution zone. Around the tube is a 10 cm diameter glass sleeve E, supported by a carriage F constituting the zone heater. The sleeve is divided into two compartments by means of three rubber gaskets; through one compartment, G, hot water flows in a closed circuit from a thermostat, and through the other, H, cold water flows. The carriage can be displaced along the tube by an electric motor winding-string around the drum I. The string is kept taut by a counterweight J. The tube itself is tilted by lengthening two of the table legs.

2.2. The Open Tube System

In this system the solute A is contained in a stainless steel tube, 6 cm in diameter and 220 cm long, B, having a longitudinal upper channel 1 cm in

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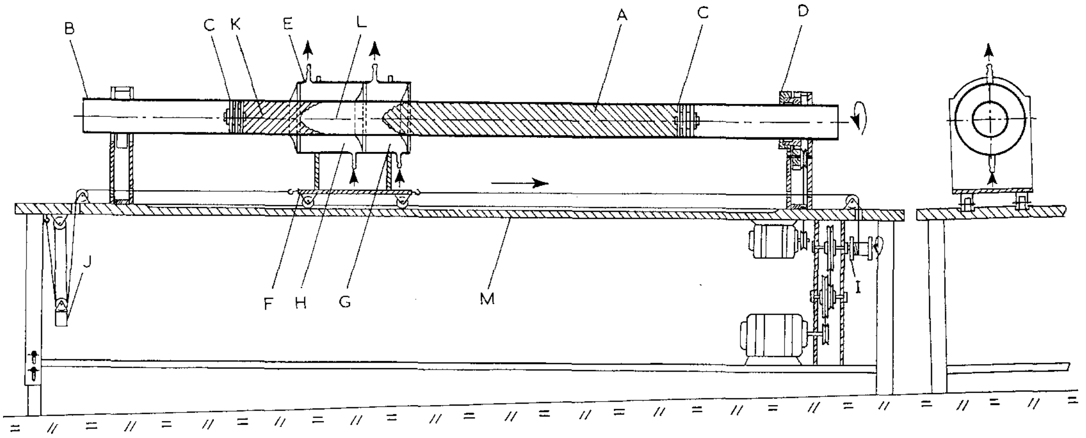

Figure 1 A longitudinal and a transversal section through the tube, heater and installation table for the closed tube system. A, the solute to be purified; B, tube of glass; C, bungs of rubber; D, cog; E, sleeve of glass; F, carriage; G, the heating compartment; H, the cooling compartment; I, drum: J, counterweight; K, the purified solute; L, the solution zone; M, the installation table.

breadth and 200 cm long, as shown in fig. 2. As in the closed tube system, the solute is enclosed in the tube by two rubber bungs, C. A 10 cm diameter stainless steel sleeve, E, supported on a carriage F, constitutes the zone heater. Two rubber gaskets delineate a compartment, H, through which cold water flows and a heating compartment, G, containing a 400 W CrNi resistance. The carriage can be moved along the tube as in the other system. In this case the solution zone L is not stirred by rotating the tube, but by two helical stirrers N placed in the solution zone.

The dissolution temperature is controlled to within ± 2° by adjusting the resistance heater, in compartment G, by means of a contact thermometer, O, placed in the solution zone. As the tube is open it is necessary in this system to keep it horizontal.

2.3. Comparison Between the Two Systems

Experiments on the THZR process using both variants showed the closed tube system to have the following advantages:

It has a temperature distribution with cylindrical symmetry which implies a symmetrical

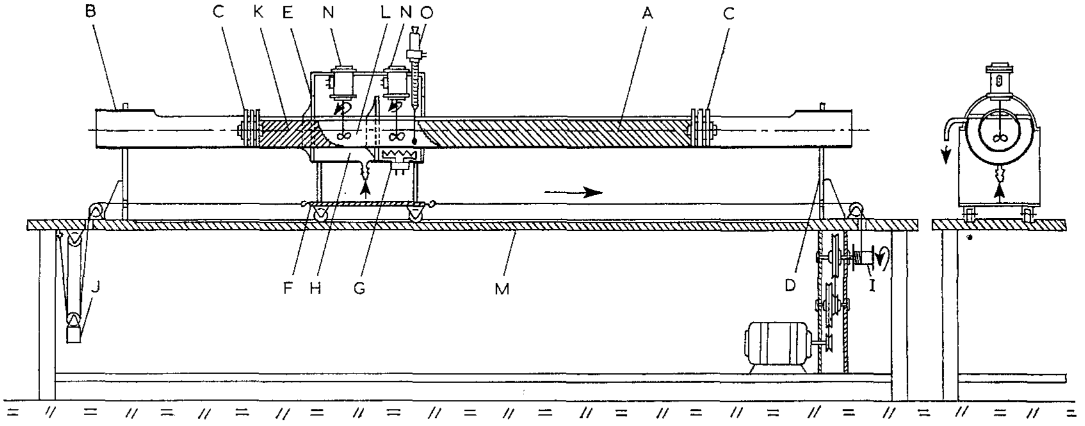

Figure 2 A longitudinal and a transversal section through the tube, heater, stirrers and installation table for the open tube system. A, the solute to be purified; B, tube of stainless steel; C, bungs of rubber; D, supports; E, sleeve of stainless steel; F, carriage; G, the heating compartment; H, the cooling compartment; I, drum; J, counterweight; K, the purified solute; L, the solution zone; M, the installation table; N, helical stirrers; O, contact thermometer.

profile of the axial section at the trailing edge face with respect to the tube axis, as shown in fig. 3a. As a consequence, in the transverse section of the crystallisate, although there are compositional variations, a better homogeneity is achieved than with the open tube system (where A and B form a solid solution with $k < 1$ or a eutectic, the crystallisate is purer at the periphery than at the tube centre. The open tube system has a temperature distribution symmetrical only with respect to the vertical plane of the axis. The profile of the vertical axial section at the trailing edge has the form of fig. 3b and the horizontal axial section of fig. 3c. Due to these profiles the transverse section shows a compositional inhomogeneity. (Where A and B form a solid solution with $k < 1$ or a eutectic, the crystallisate is also purer at its periphery than at its interior but in addition becomes more impure from the bottom of the tube to the top channel).


(a) (b) (c)

Figure 3 (a) An axial section through the tube at the trailing edge for the closed tube system. (b) A vertical axial section through the tube at the trailing edge for the open tube system. (c) A horizontal axial section through the tube at the trailing edge for the open tube system.

The zone is stirred in the laminar region by rotating the tube at 4 to 10 rev/min whilst it is tilted at a slope of 1:20. Thus, solution streams of different concentrations occur in the zone, favouring solute transport along the zone. For the open tube system helical or blade stirrers are used at speeds of 60 to 200 rev/min, which is in the turbulent region, so that stirring is not uniform along the zone. Circulation within the solution zone is greatest near the leading edge, as well as along the temperature gradient down the tube, and is least near the trailing edge, hence the cold solution streams from the trailing edge, which are deficient in solute, are prevented from reaching the leading edge. This inconvenience has been alleviated by intermittently removing solution layers from the trailing edge and transferring them towards the leading edge by means of a mini pump, whilst keeping the rotation speed at the lower limit. In this way solute transport along the zone has been improved.

The temperature gradient from the heater is steeper along the glass tube than along the stainless steel tube, thus favouring solute transport in the closed tube system. The possibility of a more rapid removal of heat through the stainless steel tube wall of the open tube system would not improve matters because the crystallisation rate, i.e. the rate determining the solution zone shift and consequently the heater movement, is smaller than the rate of heat loss through the glass tube wall.

Tilting the tube, apart from the fact that it improves the solute transport along the zone, has two definite advantages (in the case in which A and B form a solid solution with $k < 1$ or a eutectic). Firstly, the impure solution kept in the crystallisate flows back from it and secondly, any small impure crystals detached from the leading edge that have a tendency to circulate in the solution zone, since they are relatively heavy, fall back towards the leading edge where they are dissolved. In the open tube system these small crystals cannot be prevented from reaching the trailing edge before dissolving so they may be included in the crystallisate thus contaminating it. Also, the solution zone covers a large part of the surface contaminating the crystallisate.

As a result of the thermal conditions, solution zone circulation and the tilt of the tube, higher purities can be obtained using the closed tube system.

In addition, the open tube system has the disadvantage of solvent evaporation during the zone passage necessitating the addition of solvent and entailing an increase in the concentration of impurities in the crystallisate that may be present in the solvent. Also, when cracks appear in the crystallisate or in the solute, the solution zone fills them up leading to an increased consumption of solvent and increased contamination, and since the tube is open the solute may be contaminated by the surrounding medium.

However, the closed tube system shows the following disadvantages:

Filling and emptying the tube is difficult (excluding the possibility of melting the solute). The filling must be carried out so as to include as little air as possible. If the air remains in the tube it collects over the zone as it moves until it can no longer be removed. If too much air is present it prevents contact of the solution zone with the trailing edge, leading to the formation of a crystallisate in the shape of a perforated cylinder that may be contaminated in the centre.

The tube must be made of a transparent material in order to observe the process and prevent the "loss" of the zone due to a too rapid movement of the heater. The use of a glass tube involves the risk of breakage due to the differential expansion of the glass and solute.

Samples for analysis can only be taken from the tube ends after the zoning is finished, they may not be taken from along the crystallisate during the run.

3. Experimental Results

The THZR process can generally be applied to the purification of any crystalline solute subject to the following conditions:

A suitable solvent must be available in which both the solute and impurities are soluble, but which must not itself be soluble either in the crystalline solute or in the crystalline impurity. Also the solute solubility should increase with temperature. Where the solute and impurity form a solid solution, *k* should be as far as possible from unity, where they form a eutectic the eutectic composition should not consist mainly of solute and should not include trace impurities.

The solute, on crystallisation, should form sufficiently adherent crystals to delimit the trailing edge without causing solvent inclusion.

Besides these necessary conditions the following technological conditions must be fulfilled:

(*a*) the crystallisation rate should be sufficiently high to determine an acceptable rate of heater movement. High crystallisation rates can be obtained by decreasing the crystallisation temperature close to the solvent melting temperature, and by increasing the dissolution temperature close to the solvent boiling temperature. For a certain solute the crystallisation rate is higher the greater the difference between the solute solubility at the dissolution and crystallisation temperatures. However, such an increase in the crystallisation rate was shown, in the first part of this work, to decrease the purification efficiency. Increasing the solution zone convection will increase the crystallisation rate but the stirring does not diminish the temperature gradient along the zone.

(*b*) the solute, impurity and solvent should not react with the tube container or the bungs at each end. They should be stable at the dissolution temperature, and for the open tube system should not have high vapour pressures.

As some solvent remains in the crystallisate after the process, it must be possible to eliminate solvent traces from the purified material or else their presence should not be significant.

We consider the main application of the process to be in the purification of inorganic salts soluble in water. The majority of inorganic ionic salts either have high melting points, thus becoming very corrosive, show high vapour pressures or decompose or sublimate on heating so that they are not suitable for purification by zone melting. However the industrial synthesis of these salts is made using an aqueous solution, so that water can be used for their purification by means of the THZR process, the water retained among the crystals can easily be eliminated by heating, and the water traces dissolved in the crystals are not inconvenient.

For many organic substances the application of this process is inconvenient because the crystallisate becomes saturated with solvent, which leads to the disappearance of the zone, or, upon crystallisation, the crystals do not adhere sufficiently to delimit the trailing edge. However, the process can be successfully applied to some multi-nucleous aromatic hydrocarbons, to their hydroxylate derivatives, to the salts of some amines and to some organic acid salts or to the acids themselves. In these cases solvent traces remaining in the solute can easily be eliminated.

The application of this process to metal or semiconductor purification is mainly limited by finding a common solvent for all the mixture components, and by the possibility of subsequently eliminating solvent traces from the purified material.

The process has been tested on inorganic salts using water as solvent. During the tests we had two objects in view: firstly comparison of the theoretically derived results with those found in practice for the solute-impurity systems selected. Secondly, the determination of the purification efficiency for the impurities contained in the technical grade substances.

With these objectives in mind the following systems have been studied:

Nickel ammonium sulphate doped with iron (II) ammonium sulphate, a system which forms a solid solution.

Potassium di-hydrogen phosphate doped with potassium chloride, a system forming a eutectic.

Technical grade di-sodium hydrogen phosphate, copper sulphate and ammonium alum up to reagent grade.

3.1. Purification of Nickel Ammonium Sulphate Doped with Iron (II) Ammonium Sulphate

The solubility of mixtures of picromerites, double sulphates of the type $Me_2^{I}Me^{II}(SO_4)_2 \cdot 6H_2O$, has been studied at a temperature of 25°C by Hill *et al* [2] and at 20°C by Gorstein and Silanteva [3]. The mixtures of picromerites generally form solid solutions where $Me^{I} = NH_4^+, K^+, Rb^+, Cs^+$ or Tl^+ and $Me^{II} = Mg^{++}, Co^{++}, Ni^{++}, Fe^{++}, Zn^{++}, Cu^{++}, Mn^{++}$ or Cd^{++}.

The picromerites crystallise in the monoclinic system as stable hexahydrates and they only lose the crystallisation water by heating to above 100°C.

To study the case where the solute and impurity form a solid solution, we have selected from this series the system $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$—$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in which the nickel salt is considered the solute and the iron salt the impurity.

We have selected this system as its solubility has already been studied at 20°, k is less than unity for the impurity and the impurity distribution in the purified material can be easily determined using volumetric analysis.

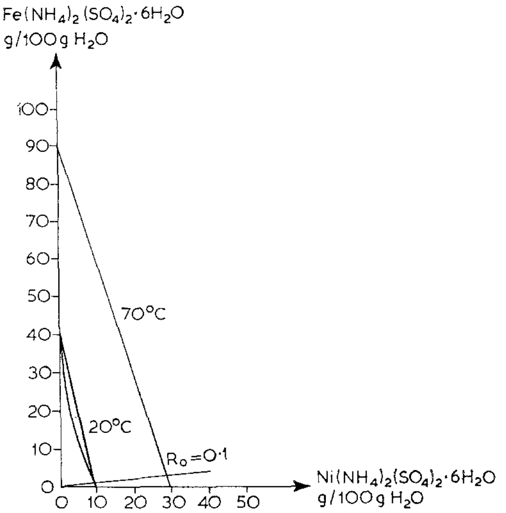

Figure 4 The ternary rectangular diagram of solubility for the system $(NH_4)_2Ni(SO_4)_2.6H_2O$—$(NH_4)_2Fe(SO_4)_2.6H_2O$—H_2O.

Fig. 4 shows the solubility curve for this system at 20°C, using data found by Gorstein and Silanteva. The dissolution straight line has been plotted using the solubility data for 70°C given by Stephen and Stephen [4].

The double salts were prepared following the

TABLE I The values of the impurity ratio along the crystallisate behind the first 6 zone passages for the system $(NH_4)_2Ni(SO_4)_26H_2O$—$(NH_4)_2Fe(SO_4)_26H_2O$ using zones of water in the closed tube system

Zone passage nr.	1	2	3	4	5	6
Co-ordinate, cm						
1.3	0.0395	0.0195	0.0075	0.0038	0.0019	0.0009
3.9	0.0525	0.0280	0.0150	0.0070	0.0038	0.0019
6.5	0.0660	0.0415	0.0220	0.0115	0.0065	0.0028
9.1	0.0810	0.0560	0.0315	0.0155	0.0095	0.0049
11.7	0.0870	0.0690	0.0405	0.0220	0.0130	0.0073
14.3	0.0910	0.0760	0.0500	0.0275	0.0170	0.0095
16.9	0.0950	0.0870	0.0650	0.0370	0.0240	0.0120
19.5	0.0980	0.0890	0.0710	0.0415	0.0270	0.0165
22.1	0.1010	0.0935	0.0760	0.0460	0.0340	0.0200
24.7	0.1	0.0970	0.0870	0.0545	0.0405	0.0240
27.3	0.1	0.1005		0.0610	0.0455	0.0270
28.6			0.0890			
29.9	0.1	0.1		0.0670	0.0500	0.0365
32.5	0.1	0.1		0.0735	0.0560	0.0395
33.8			0.0960			
35.1	0.1	0.1		0.0800	0.0670	0.0460
37.7	0.1	0.1	0.0985	0.0840	0.0735	0.0520
40.3	0.1	0.1	0.1	0.0890	0.0780	0.0650
42.9	0.1	0.1	0.1	0.0950	0.0870	0.0715
45.5	0.1	0.1	0.1	0.0995	0.0890	0.0785
48.1	0.1	0.1	0.1	0.1	0.0920	0.0825

method outlined by Mellor [5], the densities used in calculations also being taken from this paper.

Experimental work on this system was carried out using the closed tube system. The experimental method is outlined below.

The double sulphates are powdered and mixed mechanically in a ratio 10:1, nickel ammonium sulphate: iron (II) ammonium sulphate. One of the bungs (see fig. 1) is fixed at the lower end of the tube and a paste of the mixture, obtained by heating 3.8 kg mixture with 400 ml water at 100°C, is poured into the tube, settled to eliminate as much air as possible, and allowed to cool. After cooling, the paste compactly fills 100 cm of the tube. A 500 ml water zone (20 cm zone length) is added and the other bung introduced in direct contact with the water. When inserted into the apparatus the heater E is placed such that the heating compartment surrounds the solvent zone and the cooling compartment is around the empty tube. The tube is rotated and heated to a constant temperature of 70°C. As the water zone heats up the mixture of sulphates dissolve in the water and the solution volume increases until it reaches saturation. At this point the cooling water is started, and the heater motion initiated at a rate of 0.20 mm/min resulting in a concomitant shift of the solution zone through the mixture of sulphates. As the heater moves along the tube the whole mixture is dissolved and successfully crystallised. At the zone passage end the solution zone is decanted.

Each zone passage is carried out in this way. By stopping the tube rotation from time to time, the encrustation of the tube wall by solidifying crystals is encouraged and any crystals leaving the tube wall are prevented from circulating in the solution and thus are not dissolved again when near the heater.

In table I the impurity ratios along the crystallisate after each of six zone passages are given and in fig. 5 they are plotted.

To remove the samples for analysis necessitates breaking the tube so that each curve in fig. 5 represents a separate charge of the same composition. Cross sections of the purified material were taken for analysis. Samples weighing 2 g were taken from each section and dissolved in 100 ml sulphuric acid 1 N and then the iron titrated with potassium permanganate 0.1 N until the solution turns from a pale green to a colourless grey due to the absorption of Ni^{++} and MnO^{-}_4 ions.

According to the solubility values for this system we found $\alpha = 3.22$ and $\beta = 2.23$ giving $k = 0.8$. The experimental value for k was 0.35. This difference arises since we approximated the

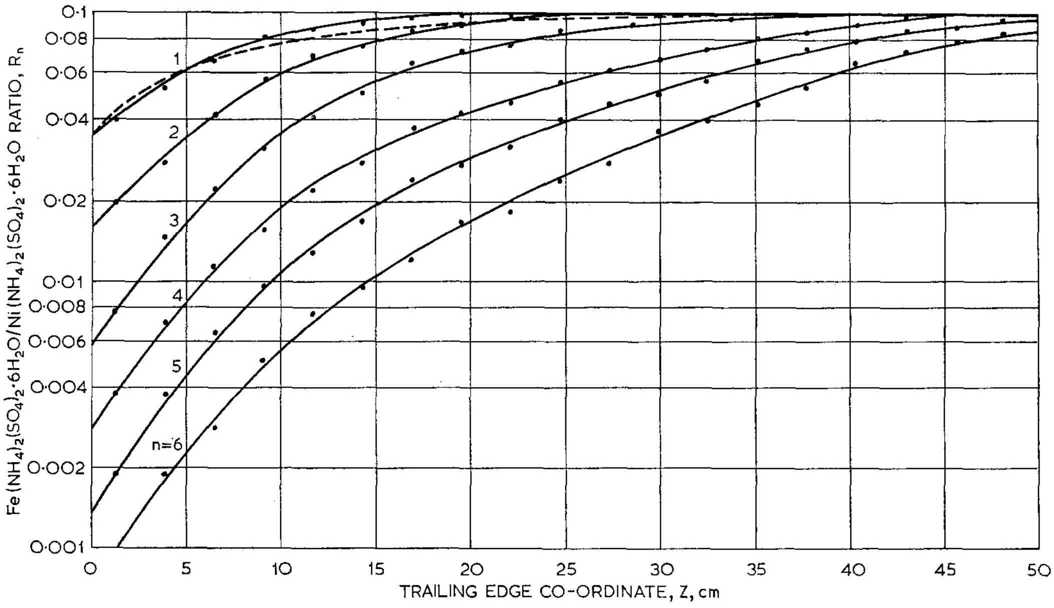

Figure 5 The distribution of the impurity ratio along the crystallisate behind the first six zone passages for the system $(NH_4)_2Ni(SO_4)_2 6H_2O$—$(NH_4)_2Fe(SO_4)_2 6H_2O$—using zones of water in the closed tube system.

solubility curves by straight lines and also assumed a direct comparison between the dissolution and crystallisation straight lines. In this case the latter assumption does not hold in practice, resulting in the variation of k with composition. Both Gorstein and Silanteva have found that the mixture does not behave ideally, in the sense that the impurity repartition constant between solid and liquid changes with composition. Experimentally the effective value of k is found to increase as the impurity ratio decreases.

In the differential equation

$$\frac{\mathrm{d}z}{L'(M - R_0)} = \frac{\mathrm{d}Y}{(R_0 - kM)Y - R_0 Y_s}$$

replacing dz (see first part of this work) by dZ where

$$\mathrm{d}Z = \frac{\rho_s l}{\rho_A L'}\left[\left\{\frac{\rho_A}{\rho_B}k - \frac{1}{M}\right\} Y - X_s\right]\mathrm{d}z$$

we obtain the equation

$$\frac{\mathrm{d}Z}{l(M - R_0)} = \frac{\frac{\rho_S}{\rho_A}\left[\left(\frac{\rho_A}{\rho_B}k - \frac{1}{M}\right) Y + Y_s\right]}{(R_0 - kM)Y - R_0 Y_s}\,\mathrm{d}Y$$

This equation relates the impurity content of the solution zone to the co-ordinate of the trailing edge. For $k = 0.35$, $\rho_A = 1.92$ g/cm³ $\rho_B = 1.86$ g/cm³, $M = -3$, $X_s = 0.298$, $Y_s = 0.898$, $l = 20$ cm and $R_0 = 0.1$ this equation becomes

$$-\frac{\mathrm{d}z}{20} = \frac{1.12Y + 0.48}{1.15Y - 0.0898}\,\mathrm{d}Y$$

and after integrating from 0 to Z and from $Y_0 = 0.029$ to Y we get

$$-\frac{Z}{20} = 0.977\,(Y - 0.029) + 1.131\log(1.59 - 20.4Y) \qquad (1)$$

Using this equation, together with $R = kY/X$ and the equation of the dissolution straight line ($X = 0.299 - Y/3$), different values of the impurity ratio as a function of the co-ordinate Z have been calculated for the first zone passage, and are shown in fig. 5 by the dashed curve. From fig. 5 it can be seen that the experimentally determined impurity ratios agree satisfactorily with the calculated values, except at the extremities of the curves. The experimental values of the impurity ratio approach the initial value faster than predicted by equation 1, owing to the appearance of a super-concentration at the trailing edge which moves with a finite rate while the zone advances, leading to an increase in the effective value of k towards unity.

For successive zone passages the curves of impurity ratio, against trailing edge co-ordinate have not been calculated owing to the mathematical difficulties. However, the shape of the experimental curves agree qualitatively with the curves calculated using equation 52 (part 1) and which are represented for a particular case in fig. 11 (part 1).

As it happens, the pursuit of a quantitative agreement between the experimental and calculated values would no longer be justified since k is dependent on concentration for this system and, similar to the case of zone melting, the effective value of k differs from equilibrium as the zone passage proceeds at a finite rate.

3.2. Purification of Potassium-di-hydrogen Phosphate Doped with Potassium Chloride

To study the case where the solute and impurity form a eutectic we have selected the system KH_2PO_4—KCl in which we consider the phosphate as solute and the chloride as impurity. The solubility of this system has been studied by Krasilsicov [6] for 25 and 50°C. Fig. 6 shows the solubility curve for 25°C using his data. The dissolution straight line has been plotted using the solubility data for 90°C given by Stephen and Stephen [4], the inversion point of the solubility curve at 90°C being determined by us as $P_E(0.146,\ 0.478)$. The solubility curve is typical of the case where a eutectic forms and not a compound. This system was selected as k can easily be measured by volumetric analysis.

Using this system the process has been carried out with both types of apparatus. Using the

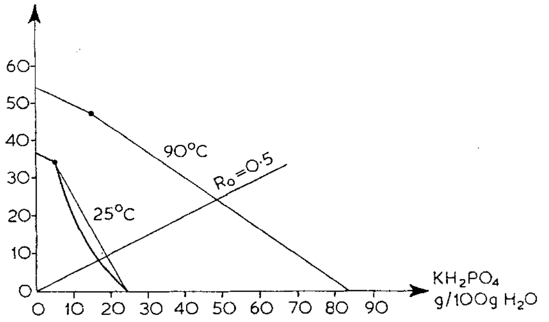

Figure 6 The ternary rectangular diagram of solubility for the system KH_2PO_4—KCl—H_2O.

closed tube system the process is similar to that used in the purification of nickel ammonium sulphate. In this case the initial mixture of phosphate and chloride is made in a ratio of 100:7. The paste is made using 5 kg of mixture and 500 ml of water which filled 115 cm of the tube. 300 ml of water (i.e. 12 cm in length) are used for the water zone. The temperature is controlled at 90°C and the solution zone travel rate is 0.33 mm/min.

Table II gives the values of the impurity ratio at the beginning and end of the crystallisate after each of five zone passages and fig. 7 gives the plot of these values. Samples for analysis were taken only from the ends of the crystallisate. As before, two samples, each weighing 2 g, are taken from the crystallisate, dissolved in some water and then suitable volumes of solution, between 1 and 20 ml, are diluted to 100 ml. The phosphate is titrated with KOH 0.1 N until phenolphthalein turns a weak pink, and separately, the chloride is precipitated with $AgNO_3$ 0.1 N in a solution acidified with nitric acid together with nitrobenzene, and then the excess silver nitrate is titrated with NH_4SCN 0.1 N using iron ammonium alum as indicator, following Volhards method [7].

TABLE II The values of the impurity ratio at the beginning and at the end of the crystallisate behind the first five zone passages for the system KH_2PO_4–KCl using zones of water in the closed tube system

Zone passage nr.	Impurity ratio at the beginning of the crystallisate	Impurity ratio at the end of the crystallisate
0	7×10^{-2}	7×10^{-2}
1	2×10^{-3}	4×10^{-3}
2	4×10^{-4}	6.6×10^{-4}
3	1×10^{-4}	1.6×10^{-4}
4	2×10^{-5}	3×10^{-5}
5	8×10^{-6}	1×10^{-5}

After the first zone passage the concentration of the chloride decreases by less than 0.5%. The analysis has been made according to the standards for the analysis of reagents [8] and [9]. One gramme of crystals is dissolved in 20 ml water, 2 ml nitric acid is added and then 1 ml of $AgNO_3$ 0.1 N. The turbidity obtained is comparable with that of a witness test containing different known quantities of chloride after leaving for 5 min. The purification efficiency is remarkable.

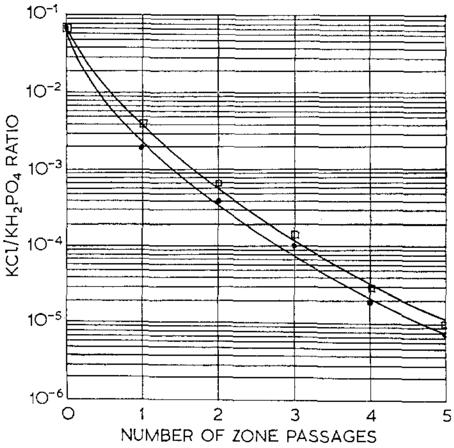

Figure 7 The dependence of the impurity ratio from the number of zone passages for the system KH_2PO_4—KCl using zones of water in the closed tube system. Values for the beginning of the crystallisate. □ Values for the end of the crystallisate.

The mode of operation using the open tube system is described below. A mixture of phosphate and chloride, weighing 2.9 kg, in a ratio of 2:1 is made. The bungs are fixed 70 cm apart in the centre of the tube and the mixture, in the form of a paste is poured along the tube using a prismatical funnel. On cooling, the tube is densely filled. A 400 ml water zone is introduced at the end nearest the beginning of the zone passage. The heater E is positioned as in the other system, the stirrers are started and the heater maintained at 90°C. As the water zone heats up, part of the mixture dissolves and the solution volume increases until it reaches saturation. The cooling water is started and the heater motion initiated at 0.5 mm/min, causing the solution zone to move through the mixture of salts. As before this motion causes the whole mixture to be dissolved and successively crystallised. After the zone passage the solution zone is decanted.

Table III gives the values of the impurity ratio along the crystallisate after each of three zone passages and on fig. 8 these values are plotted. Samples for analysis were taken using a 8 mm diameter proof stick.

The relation (see part 1)

$$\frac{Z_e}{l} = \frac{\rho_S}{\rho_A}(GY_e - X_S)$$

gives the co-ordinate Z_e up to which, in the selected conditions, the impurity concentration in the crystallisate is zero, i.e.

$\rho_A = 2.338$ g/cm^3, $R_0 = 0.5$, $M = -0.735$, $G = 3.36$, $Y_e = 0.345$, $X_S = 0.835$ and $l = 20$ cm give $Z_e = 2.78$ cm.

In the differential equation

$$\frac{dY}{G(Y - Y_e) - (X_e - x_e)} = \frac{1}{G}\frac{dz}{L}$$

replacing dz by dZ, where

$$dZ = \frac{\rho_S}{\rho_A}\frac{l}{L}\left[\left(\frac{1}{M} + \frac{\rho_A}{\rho_B}\right)(Y - Y_e) + X_e - x_e\right]dz$$

we obtain the equation

$$-\frac{1}{G}\frac{\rho_A}{\rho_S}\frac{dZ}{l} = \frac{\left(\frac{1}{M} + \frac{\rho_A}{\rho_B}\right)(Y - Y_e) + X_e - x_e}{G(Y - Y_e) - (X_e - x_e)}\,dY$$

which relates the impurity content of the zone solution to the trailing edge co-ordinate. For the above values of the parameters together with $\rho_B = 1.98$ g/cm^3, $X_e = 0.365$ and $x_e = 0.05$ this equation becomes

$$-\frac{dZ}{20} = \frac{-0.26Y + 0.607}{3.36Y - 1.52}\,dY$$

After integrating from Z_e to Z and from Y_e to Y

$$\frac{Z}{20} = 0.063 + 0.222Y - 0.3\log(4.22 - 9.32Y). \quad (2)$$

By means of this equation, together with $R = (Y - Y_e)/(X - x_e)$ and the equation of the dissolution straight line ($X = 0.835 - 1.36Y$), the impurity ratio as a function of Z has been calculated for the first zone passage and is shown in fig. 8 by the dashed curve.

TABLE III The values of the impurity ratio along the crystallisate behind the first three zone passages for the system KH_2PO_4–KCl using zones of water in the open tube system

Zone passage nr. Co-ordinate cm	1	2	3
0	0.087		
1		0.065	0.056
3	0.160		
5	0.230		
6		0.079	0.067
7	0.310		
10	0.390		
12		0.115	0.070
13	0.450		
16	0.495		
18		0.245	0.078
21	0.495		
24		0.250	0.066
26	0.495	0.325	
30		0.365	0.100
31	0.495		
34		0.385	
36	0.495		0.140
41	0.495		
42		0.480	0.165
48			0.175
51		0.495	
54			0.250
56		0.495	
60			0.275

As can be seen in fig. 8, the experimental curve follows qualitatively the shape of the calculated curve. Quantitatively, however, for the first half of the curve impurity ratios, greater than those

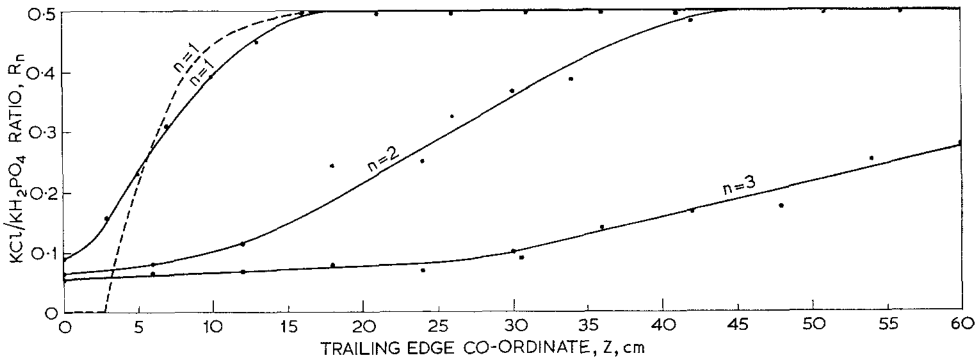

Figure 8 The distribution of the impurity ratio along the crystallisate behind the first three zone passages for the system KH_2PO_4–KCl using zones of water in the open tube system.

calculated, are found and for the second half ratios smaller than those calculated. This is due to the shape of the trailing edge which deposits oblique layers with respect to the tube axis, so that the analysed sample is a mean of crystals of different compositions, and its impurity ratio increases from the bottom to the top. In addition, the impurity ratios at the beginning of the zone passage are greater than those calculated to be due to the solution retention among the crystals.

After the first zone passage curves of the impurity ratio against the trailing edge coordinate have not been calculated owing to mathematical difficulties. As seen in fig. 8 the curves of the impurity ratio for the second and third passages show a more pronounced levelling out so that any quantitative agreement between experiment and calculation could not be made.

3.3. Purification of Di-sodium hydrogen Phosphate, Copper Sulphate and Ammonium Alum Technical Grade up to Reagent Grade

To ascertain the efficiency of the THZR process for solutes of technical grade di-sodium hydrogenphosphate ($Na_2HPO.12H_2O$), ammonium alum ($NH_4Al(SO_4)_2.12H_2O$) and copper sulphate ($CuSo_4.5H_2O$) have been selected. The purification of these solutes has been pursued to reagent grade using the closed tube system.

With di-sodium hydrogen phosphate the insoluble content of the technical phosphate must first be removed. To do this the phosphate is dissolved in water in a ratio 2.5:1 at 85°C. The hot solution is successively filtered through funnels with porosities G2, G3, G4 and G5. The resultant solution is kept at 85°C for 62 h in quartz vessels, a sufficient time for any insoluble content which passes through the G5 filter to precipitate out. The hot solution is decanted and the water evaporated until a syrup is obtained which, upon cooling, crystallises as hydrated di-sodium hydrogen phosphate. The crystals are crushed to a mean granulation of 1 mm, made into a paste and poured into the tube.

Successive zone passages are carried out with water zones of 130 ml (5.2 cm length) at zone passage rates of 0.5 to 0.8 mm/min, the maximum rate at which the zone passage can be carried out without zone loss being 1.5 mm/min. The dissolution temperature was 90°C and the crystallisation temperature 16—20°C. The zones of impure solution are decanted and collected.

After ten zone passages using deionised water of 5×10^6 ohm.cm resistivity, di-sodium hydrogen phosphate of a quality higher than reagent grade was obtained. Reduction of the impurities were as follows: sulphates 240 times, arsen 10 times, heavy metals 7.5 times, nitrates 10 times, iron 100 times and chlorides 175 times. The analysis of the di-sodium hydrogen phosphate before and after purification is shown in table IV. The analysis has been made according to the standards for reagent analysis [8] and [9] with a mixture of samples from the beginning and from the end of the crystallisate.

TABLE IV The analysis of di-sodium hydrogen phosphate before and after ten zone passages using zones of water in the closed tube system

Impurity content % / Kind of impurities	Technical grade phosphate	Purified phosphate	Standards for reagent grade max.
Insoluble	0.04	0.002	0.005
Chloride (Cl)	0.07	0.0004	0.001
Nitrogen compounds (HNO_3)	0.003	0.0003	0.005
Sulphate (SO_3)	1.2	0.005	0.008
Arsenic (As)	0.001	0.0001	0.0002
Heavy metals (Pb)	0.003	0.0004	0.001
Iron (Fe)	0.02	0.0002	0.001
pH	9.5	9.2	8.8-9.2

The theoretical purification of di-sodium hydrogen phosphate using the THZR process under the above conditions is 92%, the practical yield, however, is only 75% as losses appear during handling, washing the crystallisate ends when introducing a new solvent zone, due to looseness of the bungs and losing some crystals when decanting the impure zones.

The purification of technical grade copper sulphate is made in a similar way to that of di-sodium hydrogen phosphate.

The copper sulphate is dissolved in water in a ratio of 1:1.5 and 90°C and the solution is acidified with sulphuric acid to a concentration of 1%. The hot solution is filtered, the water evaporated and the crystals crushed and then introduced to the tube as a hot paste. Successive zone passages using water zones of 150 ml (6 cm in length), with rates of 0.4 to 0.5 mm/min have been carried out, the maximum rate being 0.75 mm/min. The same temperature of dissolution and crystallisation have been kept. After six zone passages reagent grade quality copper sulphate is obtained. Under the above conditions the theoretical purification of copper sulphate after six zone passages is 85%, however in practice it is 74%.

Ammonium alum is also purified in a similar way. The technical grade ammonium alum is dissolved in an equal amount of water at 85°C and the hot solution is filtered and kept at that temperature for 48 h to allow any insoluble content left after filtering to precipitate out. After crystallisation the material is crushed and introduced into the tube as a hot paste. Water zones of 100 ml are used and zone passage rates of 0.8 to 1.0 mm/min, the maximum possible rate being 1.5 mm/min. Ammonium alum of reagent grade quality, is obtained after five zone passages.

Under the above conditions the theoretical purification yield is 95% and in practice it is 84%. Table V shows the analysis of copper sulphate and table VI of ammonium alum after purification.

TABLE V The analysis of copper sulphate after 6 zone passages using zones of water in the closed tube system

Impurity content % / Kind of impurities	Purified sulphate	Standards for reagent grade max.
Insoluble	0.002	0.005
Chloride (Cl)	0.0005	0.001
Nitrogen compounds (N)	0.001	0.001
Iron (Fe)	0.003	0.003
Substances not precipitated by H_2S (as sulphates)	0.004	0.1
Alkalies and Earths	0.05	0.1
Other metals (Ni)	0.002	0.005

TABLE VI The analysis of the ammonium alum after five zone passages using zones of water in the closed tube system

Impurity content % / Kind of impurities	Purified alum	Standards for reagent grade max.
Insoluble	0.001	0.01
Chloride (Cl)	0.0005	0.001
Alkalies and Earths	0.05	0.25
Arsenic (As)	0.0001	0.0002
Heavy metals (Pb)	0.0004	0.001
Iron (Fe)	0.0004	0.001

The number of zone passages was determined by the purity of the technical solute and the purity standard adopted for reagent grade quality, the number of zone passages carried out were sufficient to exceed this standard. The water zone volume was chosen in each case to give a rate of zone movement near the maximum.

An attempt has been made to shorten the total time needed for purification by increasing the rate of zone movement whilst keeping the water zone constant (an increase in water zone would lead to a decreased yield). Using rates of zone passage near the maximum, we did not find a significant deterioration in efficiency of the zone passage since the differences between the rates used and the maximum rates were small and the maximum rates themselves are relatively small compared to the rates of motion of different layers of the solution through convection.

4. Conclusions

From the experimental use of the THZR process we may draw the following conclusions:

(*a*) Theoretical calculations of impurity distributions are completely confirmed on a qualitative basis. Quantitatively however, unavoidable differences exist between theory and experiment due to the inaccuracies of the simplifying assumptions adopted and to the impossibility of ever achieving ideal conditions as assumed in the theoretical analysis. In addition some errors can appear in the solubility data when establishing the temperature and when taking the samples for analysis.

(*b*) The process can be successfully applied to the advanced purification of many substances, especially inorganic salts. Its practicability is conditioned by finding a suitable solvent and by the adherence of the crystals to delineate the trailing edge. Reagent grade substances can be obtained after a relatively small number of zone passages.

(*c*) As the process is based on the purification accompanying crystallisation from solution it can be applied to the purification of any impurity, but the possibility and efficiency of such purification can only be estimated for each impurity by knowing the appropriate ternary solubility diagram.

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