FRACTIONAL CRYSTALLIZATION

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It is often desired to separate a mixture of two salts getting both pure. By fractional crystallization from a solution at constant temperature it is rarely possible to effect a complete separation. Let us suppose the simplest case, in which the salts form no compounds and no solid solutions. For each temperature there will be a definite concentration for the solution in equilibrium with the two salts as solid phases. If the original solution or mixture contained relatively more of either salt than the monovariant system that excess can be recovered. Since the relative proportions of the two salts in the saturated solution usually varies with the temperature it is possible, by repeated crystallization at two different temperatures, to obtain a complete separation. Theoretically this would require an infinite number of operations and it becomes desirable to have some definite statement of the general conditions governing such conditions that one may be able to form some idea of the least number of operations in which a given percentage separation can be obtained. Since working at high temperatures presents certain experimental difficulties it is also important to be able to estimate how much one is losing in efficiency by working at 50° , let us say, instead of at 100° . The present paper is intended to fill some of these gaps in our knowledge of this subject. It was also deemed advisable to study the effect of partial precipitation with alcohol since it would certainly be possible to change the relative concentrations of the two salts in this way and there are no data illustrating this point.

Ordinary ninety-five percent alcohol was treated with anhydrous copper sulfate until a test portion did not color the salt even after standing some time. The alcohol was then filtered

from the copper sulfate and distilled from metallic sodium, taking precautions to prevent absorption of moisture from the atmosphere. The distilled product was preserved in a glass-stoppered bottle. The salts used, potassium chlorid, potassium nitrate, sodium chlorid and sodium nitrate, were freed from their impurities—KCl and NaCl from sulfates, KNO_3 and NaNO_3 from chlorids—by repeated crystallization. After each crystallization the mother-liquor was decanted and the crystals sucked dry with the water-pump. The ordinary distilled water of the laboratory was used both in this work and in the solubility determinations. In each case, after purification, the salt was dried thoroughly in an air bath, pulverized and put in a glass-stoppered bottle.

Solubility determinations were made at 25° and at 80° in pure water and at 25° in forty percent aqueous alcohol. The salt pairs were potassium chlorid and potassium nitrate, potassium chlorid and sodium chlorid, potassium nitrate and sodium chlorid, sodium nitrate and sodium chlorid. Potassium nitrate and sodium nitrate were not taken owing to the difficulty in analyzing the solutions while potassium chlorid and sodium nitrate are the instable pair.

Bottles of about 30 cc with rubber stoppers were used for holding the solutions. Both bottles and stoppers were always cleaned carefully and dried. In all measurements an excess of each salt was weighed out roughly into the several bottles and then the desired amount of solvent added, twenty cubic centimeters with forty percent alcohol and fifteen with pure water. The forty percent alcohol was made by weighing out carefully the required amount of absolute alcohol and water. The two were mixed thoroughly and distributed at once among the several bottles, which were immediately closed tightly with rubber stoppers. To ensure complete saturation the bottles were first suspended for three hours in water kept just above thirty degrees. This bath was allowed to cool slowly and when it reached 28° the bottles were transferred to a constant temperature bath and there kept at 25° for about twenty-four hours. The bottles were shaken vigorously at intervals. The water in the bath

was kept stirred up by a Witt stirrer run by a Raabe turbine. One bottle at a time was taken from the bath and since the temperature of the room was but little below that of the bath no precaution was taken to prevent precipitation beyond that of pipetting off the solutions as rapidly as possible. Weighed amounts of the solutions were evaporated to dryness according to the method described by Trevor¹. Each residue was dissolved in water and made up to one hundred cubic centimeters. The total amount of chlorid was determined by titration with a decinormal solution of silver nitrate using potassium bichromate as an indicator. In each titration 20 cc of the 100 cc solution were used. The amounts of the nitrates are equal to the differences between the residues and the total chlorids. In the determinations at 80° it was not found necessary to keep the solutions in the bath more than eight hours. No pipette was used and the solutions were transferred directly to tared bottles warmed to 80°. Before weighing, these evaporating tubes were allowed to cool. The residues were dissolved in water and made up to five hundred cubic centimeters of which twenty-five were taken for titration. The results obtained are given in Tables I–III. In Table I, under the heading “alcohol”, are given the grams of salt in one hundred grams of aqueous alcohol; under water are the grams of salt in one hundred grams of water. Since the aqueous alcohol was sixty percent water by weight, these values are ten-sixths of the values given under “alcohol”. Below the concentrations of the salt pairs are given the ratios of these concentrations. To save space the data in Tables II and III are arranged horizontally instead of vertically. The concentrations are grams of salts per hundred grams of water. The values are the mean of two independent determinations and the probable error is about one percent. The values at 80° agree only fairly with those of Étard²; the data for sodium and potassium chlorids accord well with the results of Precht and Wittgen³. The displacement of the equilibrium

¹ Zeit. phys. Chem. 7, 468 (1891).

² Ann. Chim. Phys. (7) 3, 275 (1894).

³ Ber. chem. Ges. Berlin, 14, 1667 (1881).

by addition of alcohol is in no case as large as the change produced by difference of temperature.

TABLE I
Aqueous alcohol at 25°

	Alcohol	Water		Alcohol	Water
KCl	10.06	16.77	KNO ₃	13.74	22.90
KNO ₃	5.29	8.82	NaCl	15.78	26.30
Ratio	1.90		Ratio	0.87	
NaNO ₃	22.78	37.97	NaCl	12.28	20.47
NaCl	10.17	16.93	KCl	5.87	9.78
Ratio	2.24		Ratio	2.09	

TABLE II
Water at 25°

KCl	KNO ₃	Ratio	KNO ₃	NaCl	Ratio
34.12	22.58	1.51	41.14	38.53	1.07
NaNO ₃	NaCl	Ratio	NaCl	KCl	Ratio
43.66	26.58	1.64	29.05	17.1	1.70

TABLE III
Water at 80°

KCl	KNO ₃	Ratio	KNO ₃	NaCl	Ratio
40.20	117.5	0.361	168.8	39.81	4.14
NaNO ₃	NaCl	Ratio	NaCl	KCl	Ratio
121.6	17.62	6.90	26.5	31.0	0.855

In considering the theoretical side of the question of fractional crystallization¹, it will be better to begin with the case where we have water as solvent and work at different temperatures, taking up later the complications introduced by the alcohol. Let A and B be the amounts of the two salts in any given quantity of water at the temperature T when the solution is saturated with respect to both salts. Let A₁ and B₁ be the corresponding values at the temperature T₁. Let A/B = x and A₁/B₁ = y and we will assume temporarily that x > y. If we

¹ I am indebted to Professor Bancroft for the theoretical treatment.

pass from the temperature T to T_1 , subtracting or adding enough water to keep the second salt from dissolving or precipitating, the concentration of the second salt has thus been changed from B to B_1 , the absolute amount in solution being the same. Since the amount of the first salt is still A grams some must precipitate and equilibrium will be reached when the amount in solution is $B_1 y$ grams. Since $B = A/x$ by definition, the final amount of the first salt in solution will be $A \frac{y}{x}$ grams. If we bring the system back to the temperature T adding or subtracting enough water to keep the first salt from precipitating or dissolving, we shall have a solution supersaturated with respect to the second salt and, by the same process of reasoning, we find that the amount of the second salt left in solution will be $B \frac{y}{x}$ grams. We have now come back to the original position except that the total amount of solution is less than before and we have certain amounts of the two salts in the pure state. Since the only change in the solution is a decrease in the absolute mass of the phase, it is clear that repeating the double operation will give a similar result. This can be put in a general form. If we start at the temperature T with a solution saturated with respect to both salts and pass to the temperature T_1 allowing only one salt to crystallize and pass back to the temperature T allowing only the other salt to separate, the total amounts of the two salts remaining in solution after n cycles will be

$$A \left(\frac{y}{x} \right)^n \text{ and } B \left(\frac{y}{x} \right)^n$$

where we define the double operation as a cycle. In deducing this formula it is not assumed that T_1 is higher than T nor vice-versa. It is assumed, however, that $x > y$. If we make the contrary assumption that $x < y$ the general form of the equation remains the same but we shall have for the amounts left in solution after n cycles

$$A \left(\frac{x}{y} \right)^n \text{ and } B \left(\frac{x}{y} \right)^n.$$

If we let $X =$ the ratio of x and y where X is always less than unity we may write for the amounts in grams left in solution :

$$AX'' \text{ and } BX''$$

and for the amounts in grams obtained pure—

$$A(1 - X'') \text{ and } B(1 - X''). \quad (1)$$

Expression I is the theoretical statement of the results to be obtained by fractional crystallization at two temperatures. Practically the yield would always fall short of the value calculated from the formula, owing to the impossibility of getting rid of all the mother-liquor without washing with pure water and thus dissolving some of the salt. Another source of error lies in the fact that one would always stop a little short of the point at which the solution is saturated with respect to both salts. The formula is of value in two ways. A comparison of the actual with the theoretical yield shows the degree of accuracy with which the separation is being effected. If we desire a given percentage separation we can deduce from the formula the minimum number of cycles necessary to effect this and we shall at least know that more will be needed, how many more depending on the accuracy of the work. To take a practical example it follows from my data for NaCl and KCl at 25° and 80° that very nearly half the total salts are obtained pure at each cycle. Five cycles would therefore give nearly ninety-seven percent separation. With sodium chlorid and sodium nitrate on the other hand, three cycles would give over ninety-eight and one-half percent separation, assuming absolute accuracy of work. It should be noticed that if, as is usually the case, water is distilled off on passing to the higher temperature, water must be added when coming back to the lower temperature. Knowing the total amounts of the two salts in solution at any time and the solubilities at the two temperatures it is a simple matter to figure out the amount of water to be added or subtracted each time. The progress of fractional crystallization at two temperatures is one which should always be checked quantitatively at each step and the saving in time will compensate a hundred-fold for the extra trouble involved.

If we add alcohol to a solution saturated with respect to two salts, there will be a change in the relative concentrations of the two salts and also in the absolute concentrations. We have therefore to consider the precipitated mixture of salts and the amounts remaining dissolved in the aqueous alcohol. We will suppose that the aqueous alcohol is then evaporated. The two mixtures of the two salts can each be treated with water. If carried out properly the result will be two aqueous solutions saturated with respect to the two salts, crystals of one of the salts remaining pure at the bottom of one solution and crystals of the other salt at the bottom of the other solution. The crystals can be separated by filtration, the solutions mixed and the round is complete. We will therefore define as a cycle, the partial precipitation by alcohol, distillation of the aqueous alcohol, and treating the residues with water. Let A and B be the amounts of the two salts in any given quantity of pure water, A_i and B_i the amounts in the same quantity of water to which a definite amount of alcohol has been added. If $A/B = x$, $A_i/B_i = y_i$, and $A/A_i = z$ it can be shown that the amounts left in solution after n cycles will be

$$A \left(\frac{xz - y_i - x}{xz} \right)^n \text{ and } B \left(\frac{xz - y_i - x}{xz} \right)^n \text{ if } x > y$$

or

$$A \left(\frac{y_i z - x - y_i}{y_i z} \right)^n \text{ and } B \left(\frac{y_i z - x - y_i}{y_i z} \right)^n \text{ if } x < y.$$

Letting $Y =$ the term inside the bracket we have for the amounts left in solution after n cycles :

$$AY^n \text{ and } BY^n$$

and for the amounts obtained pure

$$A(1 - Y^n) \text{ and } B(1 - Y^n) \quad (11)$$

Expressions I and II have the same form, differing only by the difference between X and Y . At the first glance it is clear that the difference between x and y_i must be very much greater than the difference between x and y for the second expression to compare favorably in results with the first, even supposing that the

two cycles involved the same amount of work. For KCl and NaCl it was found that nearly one-half the total amount of salt was purified at each cycle when crystallizing between 25° and 80°. For the same salts at 25° and using forty percent alcohol, a little more than one-thirteenth can be purified per cycle. With sodium chlorid and sodium nitrate the difference is even greater, the rate being about three-fourths per cycle for the two temperatures and one-fourteenth for the alcohol method. It seems probable that precipitation with alcohol could be employed profitably in very few cases, possibly when potassium iodid was one of the salts.

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