somewhat unimportant deviation of the slope of the line from the ideal value must also be postponed.

It has been mentioned above that a green chromous complex resulted if the solution of anhydrous chromous chloride did not take place at the lowest possible temperature. Early experiments in which the solution was prepared by pouring 0.1 *N* acid at room temperature upon the anhydrous salt led to green solutions giving true equilibrium potentials about a tenth of a volt lower than those obtained by raking anhydrous salt into chilled acid, with stirring.

Cr^{III}/Cr^{II} by analysis.	Single potential π.	Cr^{III}/Cr^{II} from π.
0.21	0.344	7.4
0.35	0.331	12.1
0.69	0.312	24.0

These points are shown on a separate curve. In other words only about three per cent. of the total chromous salt appears to be dissociated from the complex as chromous ion.

Summary.

Pure violet $CrCl_3$, partially reduced to $CrCl_2$ by purified hydrogen at 400° in quartz, was dissolved with stirring in ice-cold, 0.1 *N* hydrochloric acid. The solution, filtered into the cell, was allowed to stand over pure mercury. If all operations were conducted in hydrogen or carbon dioxide absolutely free from oxygen, the potential rose throughout two days to a constant maximum, otherwise it fluctuated irregularly. Concentrations at equilibrium were determined analytically. Referred to normal hydrogen electrode as zero, with correction for junction potentials,

$$\pi = -0.400 + 0.065 \log Cr^{III}/Cr^{II}.$$

On platinum, potentials reached a maximum about 0.16 volt lower, with evolution of hydrogen.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE DRAINAGE OF CRYSTALS.

BY NORRIS FOLGER HALL.

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In the course of an attempt[1] to separate isotopic forms of lead nitrate by fractional crystallization, a question arose as to the desirability of centrifugal drainage as a means to the speedier separation of substances of nearly identical solubilities. As no exact treatment of the matter was known to us, the following discussion was developed, and is presented here in the hope that it may interest chemists who are undertaking the separation or purification of substances by crystallization:

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[1] Richards and Hall, THIS JOURNAL, 39, 531 (1917).

Consider a system of one liquid phase which contains (a) moles of a substance A, called the "salt"—(b) moles of a substance B, called the "impurity" and more than (c) moles of a substance C called the "solvent." The solubilities and concentrations of A and B are such that when solvent is removed by evaporation until the number of moles of C reaches the value (c), a crystalline phase consisting mainly of A begins to separate. The system is then cooled through a definite temperature interval, and the two phases separated.

The composition of the crystal phase is

$$x_1a + y_1b + z_1c \text{ where } 0 < x_1, y_1, z_1 < 1$$

and that of the liquid is $(1 - x_1)a + (1 - y_1)b + (1 - z_1)c$. Let the separation be supposed imperfect (as would always be the case in practice), so that a fraction (r) of the total mass of the mother liquor remains adhering to the crystals.

The wet crystals then contain

$$x_1a + y_1b + z_1c + r[(1 - x_1)a + (1 - y_1)b + (1 - z_1)c]$$

or the relative concentration of B in the crystals of A as separated—which will be called the "Impurity Concentration,"—is

$$I_1 = \frac{[y_1 + (1 - y_1)r]}{[x_1 + (1 - x_1)r]} \cdot \frac{b}{a}.$$

After two crystallizations,

$$I_2 = \frac{[y_2 + (1 - y_2)r]}{[x_2 + (1 - x_2)r]} \cdot \frac{[y_1 + (1 - y_1)r]}{[x_1 + (1 - x_1)r]} \cdot \frac{b}{a},$$

where as before

$$0 < x_2, y_2, z_2 < 1.$$

After (n) crystallizations

$$I_n = \frac{[y_n + (1 - y_n)r]}{[x_n + (1 - x_n)r]} \cdot \frac{[y_{n-1} + (1 - y_{n-1})r]}{[x_{n-1} + (1 - x_{n-1})r]} \cdots\cdots \frac{[y_1 + (1 - y_1)r]}{[x_1 + (1 - x_1)r]} \cdot \frac{b}{a}.$$

If $x_1, y_1, z_1 = x_2, y_2, z_2 = \ldots\ldots\ldots\ldots x_n, y_n, z_n = x, y, z.$

that is if the same fraction of each substance separates in each successive recrystallization we may write

$$I_n = \left(\frac{y + (1 - y)r}{x + (1 - x)r}\right)^n \cdot \frac{b}{a}. \qquad (1)$$

This would only be strictly true if the "thermodynamic environment" in both phases remained the same during successive recrystallizations, *i. e.*, if all the solutions present remained throughout either saturated or "sufficiently dilute." In practice, no significant error will be introduced by this simplification if (1) the solubilities and concentrations of A and B are so nearly the same that the liquid always becomes saturated with B almost as soon as with A,—(this usually is approximately true where recourse is had to fractional crystallization); or if (2) the concentration of B is so small in the crystal phase even from the first, that its subsequent elimination has little effect on the composition of the crystals. (This is the case where a moderately pure salt is being finally purified by recrystallization.)

It may often be desirable to calculate—for a particular system—the relative purifying efficiency over a chain of recrystallizations of two different methods of separation;—as, for instance, whirling in the centrifugal machine and mere drainage by gravity.

To find how many crystallizations with the less efficient drainage are equal in purifying effect to *one* crystallization with the more complete separation, we must find the condition when the "Impurity Concentrations" are equal, *i. e.*, when $I_n = I_1'$

$$\text{or } \left\{\frac{y + (1 - y)r}{x + (1 - x)r}\right\}^n \cdot \frac{b}{a} = \left\{\frac{y + (1 - y)r'}{x + (1 - x)r'}\right\} \cdot \frac{b}{a}$$

$$\text{or } n = \frac{\log\left\{\dfrac{y + (1 - y)r'}{x + (1 - x)r'}\right\}}{\log\left\{\dfrac{y + (1 - y)r}{x + (1 - x)r}\right\}}. \qquad (2)$$

[The plain letters refer to the *less* efficient (gravitational), the prime to the *more* efficient (centrifugal) drying.]

Since x and y are easily calculable in any given case from the solubilities of the substances studied, the usefulness of the formula depends on the assignment of correct values to r and r'. These will, of course, be different for every different system and for all variations of drainage technic. However, since in spite of these variations, both r and r' will probably always remain roughly of the same order of magnitude, the study of a few typical cases would supply all the information needed to assign satisfactory approximate values to these constants for any new case.

The only definite information on these points known to me is contained in a "Note on the Efficiency of Centrifugal Purification"[1] by Theodore W. Richards, who suggested the desirability of the present mathematical discussion.

The paper (which should be consulted for details), describes experiments in which sodium nitrate was variously drained and washed after crystallization from a nitric acid solution, and the separated crystals analyzed acidimetrically.

(*a*) **Calculation of *r*.**—Since the first mother liquor, which must have contained practically all the original nitric acid, was about half normal, its total volume

$$v = \frac{(15)(0.68)(1000)}{31.5} = 324 \text{ cc.}$$

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[1] Richards, This Journal, **27**, 105 (1905).

Now since 3.5 cc. were retained by each 10 g. of crystals, 24 × 3.5 or 84 cc. must have been retained by the whole mass of crystals separated. This is 84/324 or 0.259 of the total volume (or mass) of the mother liquor. (In round numbers, we may set $r = {}^1/_4$.)

(*b*) **Calculation of r'.**—On page 106 the author states that after two crystallizations with centrifugal drainage and washing, the salt contained 10^{-6} parts of impurity. From this information r' may be calculated by substitution in Equation 1.

$$(0.02)\left(\frac{r'}{0.56 + 0.44r'}\right)^2 = 10^{-6},$$

or

$$r' = 0.0040.$$

(Here y is taken $= 0$, since the proportion of the total nitric acid which forms a true solid solution in the sodium nitrate must be negligible. x as given in the paper is 240/450 or 0.53, while calculation from the solubility curve for the interval 0—100° gives 0.58. The mean value $x = 0.56$ is taken. Since the original mixture was a solution of the salt with 2% of impurity, $b/a = 0.02$.)

On the other hand, from the statement on p. 105,[1] that the amount of impurity retained by the centrifugally separated salt was about 0.05 that held when gravitational drainage was used, one is led to give r' the value $0.05\,r$ or 0.0125.[2] The mean of these values is 0.008, which is henceforth adopted as the value of r'. Substitution for r and r' in Equation 1 gives

$$I'_2 = 4.10^{-6} (1.10^{-6} \text{ found})$$

and in Equation 2 gives

$$n = 4.5 \ (4.5 \text{ found}).$$

Since the values of r and r' will not be the same for other systems and other ways of drying, the formula can at best give only an approximately quantitative indication of the magnitudes of the effects it is desired to compute. Nevertheless it has been thought worth while to prepare the accompanying table from which the chemist can tell at a glance, if he knows the solubilities of his substances, whether a great increase in speed of purification will result from thorough separation of crystals and mother liquor. The table gives the values of n, that is to say, the number of crystallizations with drainage such that one-fourth of the mother liquor remains adhering to the crystals, which will be necessary to attain the degree of purity secured by *one* crystallization where all but 0.008 of the mother liquor is removed. This is calculated for values of x (the fraction of the salt which comes out during the cooling), varying from $x = 0.01$ to $x = 0.99$, and for values of y ranging from 0 to $0.99999x$. (It will be remembered that y is the fraction of the total impurity present which

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[1] Richards, *Loc. cit.*

[2] The reason for this wide difference is, of course, the fact that no attempt was made to maintain rigorously the conditions of the experiment.

comes out as an integral part of the solid phase—inseparable from it even by perfect drainage.) For simplicity's sake, only those values of n are given in the table for which the values of y and x have a simple numerical ratio, and this ratio, y/x, is given in the top line of the table. I have called it the "inseparability "of the substances.

TABLE OF VALUES OF n.
"Inseparability" = y/x.
"Insolubility coefficient" of salt = x.

x.	$y/x = 0$.	10^{-3}.	10^{-2}.	10^{-1}.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.	0.99999.
10^{-2}	27.1	27.1	27.1	26.1	25.0	23.9	22.6	22.4	21.4	20.8	20.7	20.6	...
10^{-1}	11.1	11.1	6.8	6.4	6.0	5.7	5.4	5.1	4.8	4.5	4.4	4.2	3.2
0.2	6.9	6.9	6.5	5.4	4.9	4.6	4.1	3.5	3.0	2.8	2.8	2.8	2.8
0.3	5.7	5.7	4.9	4.3	3.8	3.5	3.2	2.9	2.6	2.4	2.4	2.4	2.4
0.4	4.8	4.8	4.3	3.2	2.7	2.4	2.3	2.2	2.1	2.0	2.0	2.0	1.8
0.5	4.5	4.5	4.1	2.8	2.3	2.1	2.0	1.9	1.8	1.6	1.6	1.6	1.6
0.6	4.2	4.2	3.7	2.5	2.2	2.0	1.9	1.8	1.7	1.6	1.6	1.6	1.6
0.7	4.0	3.9	3.5	2.3	2.1	1.9	1.8	1.7	1.6	1.5	1.5	1.5	1.5
0.8	3.8	3.7	3.4	2.2	2.0	1.8	1.7	1.7	1.6	1.5	1.5	1.5	1.4
0.9	3.6	3.5	3.3	2.1	1.9	1.8	1.7	1.6	1.5	1.5	1.5	1.4	1.3
0.99	3.5	3.4	3.2	2.0	1.9	1.7	1.6	1.5	1.4	1.4	1.4	1.3	1.3

$$\text{Values of } n = \frac{\log\left\{\dfrac{y + (1 - y)r'}{x + (1 - x)r'}\right\}}{\log\left\{\dfrac{y + (1 - y)r}{x + (1 - x)r}\right\}}, \text{ where } r = 0.25, \quad r' = 0.008$$

The value of x depends on the cooling interval and the slope of the solubility curve. The superiority of thorough drainage is relatively much greater in the case of those substances with flat, rather than steep, curves in the chosen temperature range and also for those systems where the proportion of the impurity that comes out with the salt is small. Thus the common practice of using only gravitational drainage in the case of rare earth and similar separations is shown to be well founded, since the extra time and trouble required for centrifugal drainage would more than outweigh the relatively small gain in efficiency. On the other hand, in the separation of very dissimilar substances, especially those with flat solubility durves, the attendant great increase in the speed of purification justifies almost any amount of pains taken in washing and drainage.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

THE CONTAMINATION OF PRECIPITATES IN GRAVIMETRIC ANALYSIS: SOLID SOLUTION AND ADSORPTION *vs.* HIGHER-ORDER COMPOUNDS.

BY GEORGE McPHAIL SMITH.

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Theoretical.—As is well known, many insoluble compounds which are precipitated in the course of analytical processes possess the property of