845. *Separation Factors in Fractional Crystallisation or Precipitation of the Lanthanons.*

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The work of Hill, Durham, and Ricci on systems of two isomorphous salts and water is shown to lead to the postulate from which Doerner and Hoskins derived their logarithmic separation law, $\log [a/(a - x)] = \lambda \log [b/(b - y)]$, for separation of radium and barium. For lanthanon separation this law is now found to represent both fractional crystallisation and fractional precipitation. The value of the coefficient λ for a particular system characterises the efficiency of separation; by comparison of such values, a number of separation techniques are compared. When the value of the coefficient for a particular system is known, a calculation based on entropy considerations can be made to determine the most efficient way of using the system in an actual separation. Examples of such calculations are given, one of which is shown experimentally to lead to a greatly increased efficiency of separation.

FRACTIONAL crystallisation and precipitation were once essential to lanthanon separation and are still of use alongside the more modern techniques of solvent-extraction and ion-exchange. Although detailed accounts of some separations have been published, the absence of a theory of their operation hinders quantitative comparison of their efficiencies. Earlier workers could not develop a theory because analytical difficulties made it impossible to follow a fractionation in detail. This restriction no longer exists and the present paper discusses very detailed information about a number of separations and shows that their efficiencies can be characterised by a single logarithmic separation factor, similar to that found by Doerner and Hoskins [1] for separation of radium and barium.

Hill, Durham, and Ricci [2] discussed the system of two isomorphous salts and water,

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[1] Doerner and Hoskins, *J. Amer. Chem. Soc.*, 1925, **47**, 662.

[2] Hill, Durham, and Ricci, *J. Amer. Chem. Soc.*, 1940, **62**, 2723.

showing experimentally that, if it fell into Roozeboom's class 1,[3] the relationship at equilibrium between the molar fractions of the less soluble salt (A) in solid and liquid is approximately:

$$[N_A]_s = [N_A]_l^{1/\lambda}$$

where λ is positive and greater than 1. If there are n_A moles of A and n_B moles of B and the molar ratio of A to B is R, then, from the above, we obtain

$$\frac{R_s}{R_l} = \frac{(n_A)_s(n_B)_l}{(n_B)_s(n_A)_l} = \frac{1 - [N_A]_l}{[N_A]_l^{(1-1/\lambda)} - [N_A]_l}$$

This function tends to λ when $[N_A]_l$ tends to 1 and, for values of the latter greater than 0·5, approximates closely to the limit. The experimental results of Hill *et al.*[2] are therefore equivalent to $R_s/R_l \approx \lambda$, where λ is a constant.

These authors showed theoretically that, if the two salts form a continuous series of solid solutions by interchange of ions A and B, the equilibrium between solid and aqueous solution is described by:

$$(R_l/R_s)(f_A/f_B) = (K_A/K_B)^{1/a}(f_A/f_B)_s$$

where K_A is the activity product of the salt $A_aC_cD_d\ldots$, K_B that of the salt $B_aC_cD_d\ldots$, and (f_A/f_B) is the ratio of the activity coefficients of the ions A and B. In a salt such as lanthanon ammonium nitrate containing two near-by lanthanons, the ratios of the activity coefficients of the two lanthanon ions will be close to 1 in both solid and aqueous solution; moreover, the temperature variations of the activity products of the two salts in solid solution will be similar. The above expression, therefore, also reduces to the statement that R_s/R_l is approximately constant.

For the system of two lanthanon salts and water, both the experimental and the theoretical work of Hill *et al.* can be shown to suggest that there will be a constant relation between the molar ratios of the two lanthanons in the solid and the liquid phase. This was the relation assumed by Doerner and Hoskins[1] to hold in separation of radium and barium and shown by them to lead to their crystallisation law:

$$\ln [a/(a - x)] = \lambda \ln [b/(b - y)]$$

where a and b are the initial numbers of moles of ions A and B in solution, x and y are the numbers transferred to the crystals, and λ is a constant. Heterogeneous crystals are formed in a lanthanon crystallisation, so this relation will hold for each step in a fractionation. Because the atomic weights of the lanthanons are similar, moles can be replaced by actual weights (which may be quoted most conveniently as oxide weights) and we finally have that, in a series of crystallisations to separate A and B, the value of

$$\frac{\log\left(\dfrac{\text{wt. of A in starting material}}{\text{wt. of A in liquor fraction}}\right)}{\log\left(\dfrac{\text{wt. of B in starting material}}{\text{wt. of B in liquor fraction}}\right)}$$

for each step should be constant. If A is present in large excess and is purified by a series of crystallisations which removes a constant fraction of the starting material, the above law can be shown to lead to the conclusion that the percentage of B in either crystal or liquor fractions will fall in a geometric progression, from the term of which the value of the constant for the series may be calculated.

Mellor,[4] following Crookes, discussed fractional precipitation of lanthanons from acid solution and arrived at a similar expression, in which the constant was described as the

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[3] Roozeboom, *Z. phys. Chem.*, 1891, **8**, 521.

[4] Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. V, London, 1928, p. 538.

"ratio of constants whose reciprocals may be considered as representing the specific affinities of earths A and B for the acid." Both fractional crystallisation and precipitation should follow the same law, and the constant for any series will characterise the efficiency of the process for separating the components. It may be described as a "separation factor." Weaver[5] suggested another type of separation factor, but his arguments were rebutted by Callow[6] and by Salutski and Gordon.[7]

EXPERIMENTAL

The experiments done are outlined in Table 1. Praseodymium, neodymium, and samarium were estimated spectrophotometrically on a Hilger "Uvispek" instrument; cerium was estimated volumetrically, and lanthanum by difference. All material for spectrophotometric analysis was converted through the oxalate into the oxide and analysed in nearly neutral chloride solution after suppression of interference due to iron by reduction with hydroxylamine hydrochloride. Praseodymium and neodymium were estimated directly, and samarium by the "base-line" technique. The instrument had been calibrated with pure samples of the oxides. Beer's law applied up to extinctions of 1·0.

TABLE 1.

Experiments on fractional crystallisation and precipitation of lanthanon mixtures.

Expt. no.	Material treated	Method of fractionation
1	Lanthanon ammonium double nitrate made from oxide of composition: La_2O_3 58·0% Pr_6O_{11} 10·9% Nd_2O_3 29·8% Sm_2O_3 1·3%	Fractionally crystallised by adding 25 ml. of water each time, heating until all the crystals dissolved, allowing to cool undisturbed, and decanting the liquor.
2		As for expt. 1 but solution cooled rapidly with stirring and liquor filtered off.
3		As for expt. 1, with 12·5 ml. of water each time. No liquor fraction obtained.
4		As for expt. 1, with 50 ml. of water each time.
5		12·5 ml. of water used each time but further addition made to compensate for evaporation loss on heating. No rapid cooling or stirring. Liquor decanted.
6		As for expt. 5 with 25 ml. of water initially.
7		As for expt. 5 with 50 ml. of water initially.
8		As for expt. 1 with 75 ml. of water; failed to crystallise at second step.
9		As for expt. 1 with 100 ml. of water; failed to crystallise at second step.
10	Double ammonium nitrate made from above oxide with enough cerous ammonium nitrate added to give a final oxide containing 48% of CeO_2.	As for expt. 1.
11	Double ammonium nitrate made from oxide containing 84% of La_2O_3.	Fractionally crystallised with 20 lb. of water each time with rapid cooling and stirring of solution. Liquor filtered on centrifuge.
12	Double ammonium nitrate made from oxide containing 99·7% of La_2O_3.	Fractionally crystallised by adding water and boiling solution until the b. p. reached 126°, then cooling without stirring and decanting the liquor.
13	Double magnesium nitrate made from oxide containing 55% of Nd_2O_3.	Fractionally crystallised with 100 ml. of 3 : 2 HNO_3–H_2O each time. Crystals dissolved and solution allowed to cool without stirring. Liquor decanted.
14	Double magnesium nitrate made from oxide containing cerium and heavy lanthanons.	As for expt. 15 but with a larger amount of acid.
15	Nitrate solution of oxide used in expts. 1—9.	Fractionally precipitated by adding equal quantities of MgO to boiling solution, boiling for 30 min., and filtering off precipitate.
16	Sulphate solution of oxide used in expts. 1—9.	Fractionally precipitated by heating solution and filtering off precipitate.

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[5] Weaver, *Analyt. Chem.*, 1954, **26**, 474.
[6] Callow, *Research Correspondence*, 1954, No. 7.
[7] Salutski and Gordon, *Analyt. Chem.*, 1956, **28**, 138.

Normally, every fraction was converted into oxide, which was weighed and analysed. In the calculations, it is necessary to know the amount, expressed as weight of oxide, of each element at the start of the separation. Because of the indefinite nature of many crystalline lanthanon compounds and because of the techniques used to set up separations of this type, the total weight of ingoing oxide was not usually known exactly. The starting weight for each component was therefore obtained by summation of the amounts in the fractions. From these summations for each component, it was possible to calculate the composition of the starting oxide and compare this with the known starting composition. Table 2 shows these comparisons, which were generally satisfactory.

TABLE 2.

Comparison of starting compositions as estimated by direct analysis and by summation of fractions.

Expt. no.	No. of fractions	Average wt. (g.) of oxide per fraction	Composition (%) of starting oxide			
			La_2O_3	Pr_6O_{11}	Nd_2O_3	Sm_2O_3
1	12	16·4	58·0	10·9	29·8	1·3
			58·4	10·7	29·7	1·2
2	9	18·1	58·0	10·9	29·8	1·3
			55·7	11·4	31·8	1·1
4	6	37·0	58·0	10·9	29·8	1·3
			59·1	10·6	29·3	1·0
5	19	9·5	58·0	10·9	29·8	1·3
			57·9	11·0	29·9	1·2
6	9	20·7	58·0	10·9	29·8	1·3
			58·2	10·9	29·8	1·1
7	3	54·0	58·0	10·9	29·8	1·3
			59·1	10·9	29·4	0·6
10	9	22·9	30·2	5·6	15·5	0·7 *
			30·9	5·4	15·2	0·5 *
11	10	9·5 lb.	?	?	?	?
			84·2	8·1	7·6	0·1
13	10	3·25	17·7	17·7	54·7	9·9
			18·3	19·2	52·2	10·3
14	11	8·63 lb.		?	?	?
				8·0	34·8	8·6
15	9	10·1	58·0	10·9	29·8	1·3
			56·8	11·1	30·9	1·2
16	4	6·3	58·0	10·9	29·8	1·3
			57·5	10·8	30·5	1·2

For each experiment, the figures in the first row are the compositions derived by analysis of the starting material, and those in the second are obtained by summation of fraction weights and compositions.

* CeO_2 48·0% in both cases.

TABLE 3.

Fraction compositions and calculated λ factors in experiment 1.

Fraction no.	Total oxide (g.)	La_2O_3 (g.)	Pr_6O_{11} (g.)	Nd_2O_3 (g.)	Sm_2O_3 (g.)	" Didymium oxide " (g.)	λ-Factors	
							La–Di	Pr–Nd
1	13·6	1·5	1·8	9·7	0·6	12·1	2·2	1·4
2	19·5	4·0	2·8	12·1	0·6	15·5	2·2	1·4
3	16·2	3·9	2·6	9·3	0·4	12·3	2·2	1·3
4	12·0	3·0	2·1	6·7	0·2	9·0	2·2	1·3
5	16·9	6·6	2·8	7·3	0·2	10·3	2·2	1·3
6	19·4	9·7	3·0	6·5	0·2	9·7	2·4	1·3
7	16·5	10·1	2·2	4·1	0·1	6·4	2·3	1·4
8	17·7	12·8	2·0	2·8	0·1	4·9	2·6	1·3
9	12·6	10·2	1·1	1·3	—	2·4	2·5	1·3
10	17·0	15·4	0·8	0·8	—	1·6	2·5	1·6
11	16·5	15·7	0·5	0·3	—	0·8	3·1	1·2
12	19·3	19·0	0·2	0·1	—	0·3		—
Remainder	8·2	8·2	—	—	—	—		—
Totals	205·4	120·1	21·9	61·0	2·4	85·3		

In experiments 1—9, 11, 12, 15, and 16, the major components were La_2O_3, Pr_6O_{11}, and Nd_2O_3; praseodymium and neodymium are separated with difficulty (they are the classical " didymium "), so that the system can be taken, to a first approximation, as a two-component mixture of lanthanum and " didymium." In these experiments, after the summation described above, the amounts of these two components before and after each stage were determined successively. For example, in experiment 1, the summation gave the initial material as containing 120·1 g. of La_2O_3 and 85·3 g. of " Di_2O_3," and the first two fractions, which were removed in the liquor, contained, respectively, 1·5 g. and 4·0 g. of La_2O_3 and 12·1 g. and 15·5 g. of " Di_2O_3." For these two steps, λ for La–Di was then calculated as log (120·1/1·5)/log (85·3/12·1) and log (118·6/4·0)/log (73·2/15·5). Similar calculations were made, where appropriate, for the other experiments, to determine the composition of the liquid phase before and after each step and to calculate λ as above.

The values obtained were reasonably constant throughout an experiment. Factors calculated in the same way for individual components, *e.g.*, Pr and Nd, were also constant. To illustrate the results, Table 3 shows the complete results of experiment 1, Table 4 those of

TABLE 4.

Fraction compositions and calculated λ factors in experiment 5.

Fraction no.	Total oxide (g.)	La_2O_3 (g.)	Pr_6O_{11} (g.)	Nd_2O_3 (g.)	Sm_2O_3 (g.)	" Didymium oxide " (g.)	λ-Factors	
							La–Di	Pr–Nd
1	18·6	3·4	2·9	11·7	0·6	15·2	2·1	1·2
2	12·8	3·2	2·0	7·4	0·3	9·6	1·8	1·2
3	—	—	—	—	—	—	—	—
4	17·8	4·2	2·8	10·2	0·5	13·6	2·3	1·3
5	13·6	4·4	2·2	6·7	0·3	9·2	2·1	1·3
6	—	—	—	—	—	—	—	—
7	17·5	7·0	2·8	7·4	0·3	10·5	2·3	1·3
8	10·5	5·0	1·6	3·7	0·1	5·5	2·1	1·3
9	—	—	—	—	—	—	—	—
10	10·6	6·1	1·5	3·0	0·1	4·5	2·1	1·3
11	3·0	2·0	0·4	0·6	—	1·0	1·5	1·1
12	11·2	8·1	1·2	1·9	—	3·1	1·8	1·2
13	16·0	12·5	1·4	2·0	—	3·5	2·3	1·3
14	2·5	2·1	0·2	0·2	—	0·4	1·4	1·0
15	9·2	8·0	0·6	0·6	—	1·2	1·8	1·1
16	12·5	11·3	0·6	0·6	—	1·2	2·2	1·2
17	8·6	8·1	0·3	0·2	—	0·5	2·0	—
18	7·3	7·0	0·2	0·1	—	0·3	2·4	—
19	9·1	9·0	0·1	0·1	—	0·1	—	—
Remainder	8·0	7·9	—	—	—	0·1	—	—
Totals	188·8	109·3	20·8	56·5	2·2	79·5		

TABLE 5.

Fraction compositions and calculated λ factors in experiment 13.

Fraction no.	Total oxide (g.)	La_2O_3 (g.)	Pr_6O_{11} (g.)	Nd_2O_3 (g.)	Sm_2O_3 (g.)	λ-Factors		
						La–Di	La–Pr	Pr–Nd
1	2·89	0·00	0·04	0·59	2·26	—	—	1·4
2	4·29	0·03	0·09	1·27	2·90	2·2	1·2	1·4
3	3·59	0·02	0·09	1·36	2·12	2·2	1·3	1·5
4	3·39	0·03	0·14	1·83	1·39	2·1	1·3	1·5
5	2·39	0·03	0·10	1·41	0·85	1·9	1·2	1·5
6	2·95	0·04	0·19	2·16	0·56	1·9	1·3	1·5
7	3·41	0·05	0·27	2·74	0·35	2·0	1·4	1·5
8	3·35	0·06	0·30	2·81	0·18	1·9	1·4	1·5
9	2·97	0·05	0·29	2·54	0·09	1·9	1·4	1·5
10	3·30	0·10	0·36	2·79	0·05	1·8	1·3	1·5
Remainder	75·47	19·35	18·87	36·88	0·37	—	—	—
Totals	108·00	19·76	20·74	56·38	11·12			

experiment 5, and Table 5 those of experiment 13. Table 6 gives the average values of the factors in all the experiments and their maximum and minimum values. In experiments 15 and 16, lanthanum was concentrating in the liquor fraction, not in the solid, so the factors are given as reciprocals to facilitate comparison with the other results.

In experiment 12, nearly pure lanthanum was fractionated by concentrating the solution of lanthanum ammonium nitrate until it reached a constant b. p. at each step; in this way, the fraction removed in the liquor was kept reasonably constant. Table 7 shows the compositions of some of the fractions. According to the theory, the percentage impurity should fall in a geometric progression; the Table shows the calculated impurity levels on the basis of a progression of term 0·80. From this term, which fits the results very well, λ for the experiment is calculated as 1·9.

TABLE 6.

Average λ-factors in the various experiments. Maximum and minimum values are shown in parentheses after each average.

Expt.	λ-Factors				
no.	La–Di	Pr–Nd	La–Ce	Ce–Pr	La–Pr
1	2·4(2·2,3·1)	1·3(1·2,1·6)			
2	2·9(2·3,4·0)	1·5(1·3,1·7)			
4	2·9(2·5,3·6)	1·5(1·4,1·6)			
5	2·0(1·4,2·4)	1·2(1·0,1·3)			
6	2·2(1·7,2·6)	1·3(1·2,1·3)			
7, 8, 9	2·9(2·5,3·4)	1·5(1·4,1·7)			
10	2·3(1·9,2·7)	1·3(1·2,1·4)	1·4(1·3,1·6)	1·5(1·3,1·8)	
11	2·8(2·0,3·0)	1·4(1·3,1·6)			
13	2·0(1·8,2·2)	1·5(1·4,1·5)			1·3(1·2,1·4)
14		1·5(1·4,1·8)		1·4(1·0,1·6)	
15	1/3·8(3·1,4·1)	1/1·2(1·1,1·3)			1/3·3(2·7,3·8)
16	1/3·5(3·3,3·6)	1/1·4(1·3,1·4)			1/2·8(2·6,2·9)

TABLE 7.

Fraction compositions in experiment 12.

	Pr_6O_{11}	Nd_2O_3	" Didymium oxide " (%)	
Fraction no.	(%)	(%)	Found	Calc.
1	0·53	0·29	0·82	0·81
3	0·35	0·16	0·51	0·51
5	0·24	0·09	0·33	0·32
7	0·14	0·05	0·19	0·20
11	0·07	0·02	0·09	0·08
13	0·04	0·01	0·05	0·05
15	0·03	<0·01	<0·04	0·03

Initial composition of material: La_2O_3 99·73%; Pr_6O_{11} 0·19%; Nd_2O_3 0·08%.
Average fraction removed: 9%.

DISCUSSION

The results show that the separations are characterised by logarithmic separation factors. Although the value of the factor for any one series varies somewhat from step to step in some cases, the average values give an excellent indication of the progress of the separation. This is seen in Tables 8 and 9 where the calculated course of the separation is compared with experiment, equal fraction weights of the average value for the experiment being assumed and the average separation factor used. The fit is excellent.

The larger the factor between a pair of components, the better the process will be for separating those components. However, before drawing conclusions about the various systems examined, it is necessary to consider in more detail the results for the double ammonium nitrate system. Here, the factor varies greatly from experiment to experiment, λ for La–Di ranging from 1·9 to 2·9. This is because the differing conditions lead to retention of differing amounts of liquor in the crystals. Any retention of liquor would lead to a low value for λ; in the experiments giving high average values, there was more variation in the individual values, and those were always low when the fraction weight

TABLE 8.

Actual and calculated effects of separation steps on material of experiment 15.

	Actual		Calc. for equal fractions of 10·11 g. and $\lambda = 3{\cdot}8$		Calc. for max. entropy change at each step, $\lambda = 3{\cdot}8$	
Step no.	Wt. of oxide left after step (g.)	La_2O_3 (%)	Wt. of oxide left after step (g.)	La_2O_3 (%)	Wt. of oxide left after step (g.)	La_2O_3 (%)
—	104·0	56·8	104·0	56·8	104·0	56·8
1	95·3	59·5	93·9	60·1	33·6	89·6
2	86·1	62·7	83·8	63·8	17·6	97·7
3	75·0	67·3	73·7	67·8	10·0	99·6
4	63·8	72·6	63·6	72·5		
5	53·5	77·9	53·5	77·8		
6	42·5	84·0	43·4	83·6		
7	31·9	90·9	33·2	89·8		
8	21·6	95·4	23·1	95·2		
9	13·0	96·9	13·0	99·2		

TABLE 9.

Actual and calculated effects of separation steps on material of experiment 11.

	Actual		Calc. for equal fractions of 9·48 lb., $\lambda = 2{\cdot}9$		Calc. for max. entropy change at each step, $\lambda = 2{\cdot}9$	
Step no.	Wt. of oxide left after step (lb.)	La_2O_3 (%)	Wt. of oxide left after step (lb.)	La_2O_3 (%)	Wt. of oxide left after step (lb.)	La_2O_3 (%)
—	118·6	84·2	118·6	84·2	118·6	84·2
1	111·8	87·6	109·1	88·3	105·6	89·0
2	100·8	92·0	99·6	91·8	97·1	92·2
3	90·2	95·0	90·1	94·5	90·6	94·5
4	78·6	97·0	80·6	96·5	85·6	96·1
5	70·6	97·7	71·2	97·8	81·6	97·2
6	64·9	98·5	61·7	98·7	78·1	98·0
7	56·8	99·1	52·2	99·3	75·1	98·5
8	47·3	99·4	42·7	99·6	72·5	99·0
9	34·1	99·6	33·2	99·8	70·1	99·2
10	23·8	99·7	23·8	99·9	67·8	99·5

was abnormally low for the series. In experiment 1, where 25 ml. of water were used each time without stirring, λ for La–Di was 2·4; in experiment 10 (the same conditions but with Ce present) it was 2·3. In experiments 2 and 11, the solutions were stirred during cooling, which would help to reduce entrainment; and, in experiments 4, 7, 8, and 9, larger quantities of water were used, so that smaller amounts of crystals were left, which would also reduce entrainment. In these experiments, λ was 2·8 or 2·9. In experiments 5, 6, and 12, little water was used, entrainment would be high and λ was 1·9—2·2. An examination of the results shows that the larger values are not simply a function of larger liquor fractions.

Entrainment is unlikely to be serious in the fractionation of double magnesium nitrates from nitric acid or in fractional precipitation of hydroxides but might occur in precipitation of the sulphates.

Considering now the results for the different systems examined, it is possible to draw the following conclusions about the relative efficiencies of different techniques: (1) In fractional crystallisation of the double ammonium nitrates, cerium does not assist the separation of lanthanum and " didymium " (compare expts. 1 and 10). (2) Crystallisation of the double ammonium nitrates, provided liquor entrainment is prevented, gives separation factors of 2·9 between lanthanum and " didymium," and 1·5 between praseodymium and neodymium. This method gives better separation of lanthanum from " didymium " and as good separation of praseodymium from neodymium as crystallisation of the double magnesium nitrates from acid, where the separation factors are 2·0 for the former and

1·5 for the latter pair (compare expts. 2 and 4 with 13 and 14). (3) Fractional precipitation with magnesium oxide gives a better lanthanum separation than the above fractional crystallisations, the lanthanum–" didymium " factor being 3·8. It gives poor separation of praseodymium from neodymium, the factor being 1·2 (compare expts. 2 and 4 with 15). (4) Fractional precipitation of sulphates gives good lanthanum separation, the factor between lanthanum and " didymium " being 3·5, and reasonably good separation of praseodymium from neodymium, the factor being 1·4 (expt. 16).

Although conclusions such as these are valuable, it is possible to make further use of the theory by determining the most efficient way of carrying out a particular separation. Tables 8 and 9 show that, if the separation factor and fraction size are known, it is possible to calculate accurately the course of the process. It should therefore be possible to calculate the effects of alterations in fraction size on the yield or purity of the final material. In this connection, Joy and Payne [8] showed that the efficiency of a step which divides a starting material into two or more fractions should be measured by the difference in entropy between starting material and fractions, the best separation resulting in the maximum entropy decrease. A lanthanon mixture probably forms ideal or, at least, regular solutions, so that the entropy of a mixture of a moles of A and $(1 - a)$ moles of B is:

$$S = a\boldsymbol{R} \ln a + (1 - a)\boldsymbol{R} \ln (1 - a)$$

According to the theory of this paper, a separation step applied to the mixture will give a liquid fraction containing ax^{λ} moles of A and $(1 - a)x$ moles of B, the solid fraction having $a(1 - x^{\lambda})$ moles of A and $(1 - a)(1 - x)$ moles of B. By using the above expression for entropy, it can be shown that the maximum entropy decrease occurs if

$$\frac{\lambda a x^{\lambda-1}}{(1-a)} = \frac{\ln\left[\dfrac{(1-x)}{x} \cdot \dfrac{ax^{\lambda} + (1-a)x}{a(1-x^{\lambda}) + (1-a)(1-x)}\right]}{\ln\left[\dfrac{(1-x^{\lambda})}{x^{\lambda}} \cdot \dfrac{ax^{\lambda} + (1-a)x}{a(1-x^{\lambda}) + (1-a)(1-x)}\right]}$$

Although this equation cannot be solved analytically, numerical solutions can be obtained for given values of λ and a. From the resulting value of x, it is then possible to determine the required fraction size.

Such calculations can be illustrated from the results of experiments 15 and 11. In experiment 15, the starting material was 59·1 g. of La_2O_3 and 44·9 g. of " Di_2O_3," which was divided into ten approximately equal fractions of average weight 10·11 g. The expected course of this procedure can be calculated, since the starting material and the separation factor are known. The fractions are removed in the solid phase so that, after the first step, the liquid should contain (104 — 10·11) g. of oxide, the composition of which is found by solving (by successive approximation) the equation:

$$44{\cdot}9x_1^{3{\cdot}8} + 59{\cdot}1x_1 = 93{\cdot}89.$$

x_1 is found to be 0·95, from which the composition of the remaining material can be determined as 56·38 g. of La_2O_3 and 37·51 g. of " Di_2O_3." The next step is then calculated by solving:

$$37{\cdot}51x_2^{3{\cdot}8} + 56{\cdot}38x_2 = 83{\cdot}78.$$

Similar calculations can be made for each step and Table 8 shows the results of these calculations as compared with the experimental results. The calculations agree very well with the experimental results, so that we can proceed to calculate the effects of altering the fractionation conditions. By solving the equation for maximum entropy change for a starting purity of 56·8% and a separation factor of 3·8, it is found that x should be 0·51 rather than 0·95, so that the first step should be arranged to leave a liquor fraction of

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[8] Joy and Payne, *Ind. Eng. Chem.*, 1955, **47**, 2157.

composition 44·9 × $0{\cdot}51^{3{\cdot}8}$ g. of " Di_2O_3 " and 59·1 × 0·51 g. of La_2O_3, *i.e.*, 30·1 and 3·5 g., so that it would be necessary to precipitate 70·4 g. (67·7%) of the original material. The material left would have a purity of 89·6% and the value of x for maximum entropy change for the next step would be 0·57, leading to the precipitation at that step of a further 15·4%. At the third step, the calculation shows that 7·4% should be precipitated, to leave 10 g. of material of purity 99·6%. Instead of a yield of 13 g. of material after 9 steps, it should be possible to obtain 10 g. after only 3 steps, a considerable improvement in the efficiency of the process.

To check these calculations, a synthetic oxide was made up of the starting composition used in experiment 15 and about 100 g. of this was dissolved and fractionally precipitated in an attempt to follow the maximum-efficiency route as determined above. The actual amounts precipitated were 66%, 15·3%, and 8·4%, leaving 10·4% of a material 99·1% pure. The agreement was considered satisfactory and the marked improvement compared with experiment 15 is noteworthy.

Similar calculations were made for the starting material of experiment 11. In Table 9, these calculated stages are compared with the actual ones. In this case, the early stages of the actual separation agreed closely with those suggested as most efficient, but the later fraction sizes were too large. In this case, it might be difficult to remove fractions of the correct size; unfortunately, it became necessary to abandon the work at this stage so that the point could not be examined. It seems, however, clear that the technique of calculation described is capable of throwing much light on the course of a separation.

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