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EVAPORATION OF POTASH BRINES.

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INTRODUCTION.

It has long been known that many American brines, including ocean water, contain potassium along with much larger quantities of other salts, and during the last few years investigations have shown that brines from several different localities in the United States contain a high percentage of potassium. The development of an economic process for the extraction of potassium from these brines is a problem of great importance. The most practical methods so far proposed depend on evaporation and fractional crystallization. These facts suggest the desirability of knowing just what effect evaporation will have on the various constituents of a brine. Much is already known about the subject in a general way, and it is possible to predict certain qualitative relations concerning such simple salt solutions as those of sodium and potassium chlorides and also concerning solutions in general whenever the solid phases are known. Theoretically a saturated solution of sodium chloride containing a small amount of potassium chloride will deposit on evaporation only sodium chloride until the solution becomes saturated with respect to both salts; and a saturated solution of potassium chloride containing a small amount of sodium chloride will likewise deposit potassium chloride alone until equilibrium is reached. At 30° C. the saturated mixture¹ of these two salts contains 11.7 per cent of potassium chloride and 19.7 per cent of sodium chloride. On further evaporation at this temperature no change takes place in the composition of the solution, both salts being deposited in such quantities that the potassium-sodium ratios in both liquid and solid phases remain constant. Other instances of such simple relations could be given. Usually, however, solutions of two or more salts present much more complicated relations. The number of different ions present and the possible formation of other compounds, hydrates, and isomorphous mixtures are the chief factors influencing the complexity of the system. Consequently it is difficult to predict what changes will result through the evaporation of solutions containing several different ions. Furthermore, experiments with even the simplest systems do not yield the results that might be expected from a theoretical consideration. Precipitates often carry down mechanically or otherwise appreciable quantities of other salts, supersaturation may easily occur, and equilibrium is often slow in reaching its final adjustment. These are all factors of practical importance.

Experimental results relative to the changes which take place during evaporation, particularly with reference to potassium salts, are rather meager. In his evaporation studies on sea water Usiglio² found that the potassium in solution increased as evaporation proceeded, and the results of his experiments indicate in a general way what happens when sea water evaporates. However, in those early days the determination of potassium, and perhaps other constituents, was not capable of the refinement exacted in modern times. Usiglio found that the saline residue from sea water contained 0.71 per cent of potassium, while according to modern analyses³ the figure is about 1.1 per cent. Accordingly, it is assumed that Usiglio's determinations of potassium in the products of evaporation may have been likewise erroneous. Hence, it is not possible to calculate with any degree of assurance the amount of potassium which was lost by deposition from solution during evaporation. However, it appears that in

¹ Precht and Wittjen, *Deutsch. chem. Gesell. Ber.*, vol. 14, p. 1667, 1881.

² *Annales chim. phys.*, 3d ser., vol. 27, pp. 92, 172, 1849.

³ Clarke, F. W., *The data of geochemistry*, 2d ed.: U. S. Geol. Survey Bull. 491, p. 113, 1911.

concentrating the brine from 5 liters to about 100 cubic centimeters approximately 8 per cent of the potassium originally present was lost from solution. In the final mother liquor 3.31 per cent of the total salts was potassium, a condition which indicates that the potassium had still not saturated the solution, as the total salts of several sea water bitterns from the vicinity of San Francisco are reported¹ to contain 5 to 10 per cent of potassium.

Chatard² evaporated large quantities of the water of Owens Lake, Cal., which, after being reduced to the point of crystallization contained about 0.8 per cent of potassium. The experiments were carried out at the normal temperature in the vicinity of Owens Lake. A series of crops of crystals were obtained, each of which contained about 1 per cent of potassium chloride. Unfortunately the weights of the salts and the mother liquors in each experiment are not reported, and consequently the relations can not be followed in detail. Another important factor, the analysis of the final mother liquor, is also lacking. However, it is probable that the solution did not become saturated with salts of potassium because each crop of crystals contained approximately the same percentage of this constituent. This conclusion is strengthened by similar results of the evaporation studies on the water of Mono Lake, Cal.² In the experiments at Mono Lake the final mother liquor was evaporated to dryness and the residue was analyzed. The potassium-sodium ratio in this product was 0.27, which is very strong evidence that the final mother liquor was not saturated with salts of potassium, experiments recorded elsewhere in the present paper having shown that in solutions very similar to that in Owens Lake the potassium-sodium ratio may become as high as 0.59. According to Chatard's results, about 15 per cent of the potassium originally present was lost in the evaporation water of Owens Lake long before the bittern became saturated with potash salts.

Evaporation studies on artificial potash brines were undertaken by the writer in the hope of throwing further light on the conditions governing the deposition of salts from solutions. It was planned to begin the investigation with simple salt mixtures and, by gradually including other salts, to deal finally with complex brines comparable with those found in nature. Though it has been possible to do only a small part of the experimental work contemplated, it seems advisable to publish the data thus far obtained, with the hope of supplementing them later.

In conducting the experiments an attempt was made to reproduce as far as possible commercial conditions. It is not believed that equilibrium reached final adjustment in the solutions, and consequently the results can not be considered as solubility determinations.

METHODS.

PREPARATION OF SOLUTIONS.

In the preparation of the solutions pure anhydrous chemicals were used except in the experiments with borates, for which borax was employed. The required amount of each salt was weighed out and dissolved in a definite volume of water. The composition of the original solutions as recorded in the tables was calculated from the data thus obtained.

METHOD OF EXPERIMENTATION.

In the preliminary experiments 150 grams of the solution under investigation was evaporated in a small beaker on the steam bath to about one-fourth its original volume and was allowed to cool at room temperature, which was between 25° and 30° C. The solution was stirred occasionally while cooling, and care was taken to start crystallization in order to prevent supersaturation. After the solution had cooled, it was filtered from the crystals by strong suction into a small flask, weighed, and analyzed.

In all other experiments 500 to 1,000 grams of solution was evaporated in beakers at intervals on the steam bath, and the progress of the results of evaporation was watched by removing from time to time the deposited salts and weighing and analyzing the solution. After each

¹ Phalen, W. C., The salt industry of the United States: U. S. Geol. Survey Bull. — (in preparation).

² Chatard, T. M., Natural soda: U. S. Geol. Survey Bull. 60, pp. 27-101, 1888.

stage in the evaporation the solution was stirred vigorously for several hours in an electrically controlled thermostat, which deviated less than 0.05° from 30° C., until the solution attained the temperature of the bath and appeared to be in equilibrium otherwise. It was then allowed to settle, and without change of temperature a sample of it was transferred by means of a pipette to a flask and weighed. The sample was drawn out through a filter consisting of a piece of cotton held in a small funnel which was attached to the pipette by a piece of rubber tubing. The pipette had a capacity of 8.606 cubic centimeters at 20° C., and from these data the specific gravity of the solution was calculated. The main portion of the solution was filtered into a smaller beaker with strong suction, as in the preliminary experiments, care being taken to remove as much as possible of the adhering liquid from the crystals. The filtrate was then returned to the steam bath and was further concentrated to about half its volume. It was then cooled in the thermostat, filtered from the crop of crystals, and otherwise treated as described above for the first product of evaporation, the filtrate being returned to the steam bath. The concentration was similarly continued at intervals until only a small amount of liquid remained. In all the experiments the procedure above described was followed in each succeeding stage in the evaporation.

METHODS OF ANALYSIS.

The weighed samples of solution obtained by the concentration just described were diluted to definite volume, and aliquot portions representing 3 to 4 grams of solution were taken for analysis. The determinations were made in duplicate, and practically all the figures given in the tables (pp. 68, 69, 71) are the average of two closely agreeing results. Common methods of analysis were usually employed, but short cuts were taken wherever possible, and a brief description of the procedure therefore seems advisable. The sulphate radicle was precipitated and weighed as barium sulphate, and potassium was estimated by the modified chlorplatinate method.¹ Sodium was determined by weighing the combined bases as chlorides or as sulphates and subtracting the corresponding equivalent of the potassium, borates when present being first removed by repeated evaporation with methyl alcohol and hydrochloric acid. Chlorine was determined by titration with N/10 silver nitrate after neutralizing the solution with nitric acid. The borate radicle was estimated by titration of the boric acid with N/10 sodium hydroxide in the presence of mannite and phenolphthalein. The carbonate radicle was determined by titrating with N/10 hydrochloric acid in the presence of methyl orange and subtracting the borate equivalent.

The calculations were made with the slide rule, and a few of the results may differ slightly from the true amounts. The percentage of the various constituents lost during evaporation is stated in round numbers with two significant figures, and no correction was made for the amount of salts removed with the sample for analysis.

¹ Hicks, W. B., A rapid modified chlorplatinate method for the estimation of potassium: Jour. Ind. Eng. Chem., vol. 5, pp. 650-653, 1913.

EXPERIMENTAL RESULTS.

PRELIMINARY EXPERIMENTS.

In the preliminary experiments solutions nearly saturated with salts of sodium and containing much smaller amounts of salts of potassium were concentrated on the steam bath to about one-sixth their original volume, it being assumed that the resulting solutions would be approximately saturated with potash salts. The solutions were cooled at room temperature, filtered, and analyzed. The results are given in the following table, together with the composition of the original solution and other data:

Changes resulting from the evaporation of artificial potash brines containing one acid radicle.

Character of solution.	Solution before evaporation.			Solution after evaporation.					Potassium lost (per cent).	K/Na ratios.		
	Quantity (grams).	Sodium (grams).	Potassium (grams).	Quantity.		Sodium (per cent).	Potassium.			Before evaporation.	After evaporation.	Saturated solution.
				Grams.	Per cent.		Per cent.	Grams.				
KCl+NaCl.....	150	5.901	1.573	24.1	16	8.50	4.58	1.104	30	0.27	0.54	^a 0.79
K ₂ CO ₃ +Na ₂ CO ₃	150	4.882	1.698	21.3	14	9.36	6.22	1.326	22	.35	.67	-----
K ₂ SO ₄ +Na ₂ SO ₄	25	.737	.225	6.3	25	4.72	2.72	.170	24	.31	.58	-----

^a Precht and Wittjen, Deutsch. chem. Gesell. Ber., vol. 14, p. 1667, 1881.

According to these results, the potassium appears to have concentrated most rapidly in the carbonate and least rapidly in the sulphate solution, and the potassium-sodium ratio after evaporation is greatest in the carbonate solution. It is apparent from the column of ratios that the chloride solution had not become saturated with potassium, and it is probable that the other concentrated brines had not reached equilibrium. The loss of 20 to 30 per cent of the potassium during evaporation shows that a large part of the potassium is removed from such brines before the solution becomes saturated with this constituent.

ALKALI BRINES CONTAINING TWO ACID RADICLES.

In the evaporation experiments with brines containing two acid radicles the original solutions were approximately of the same strength and contained three to four times as much sodium as potassium. In each series of experiments 500 grams of the solution was evaporated in stages, and the effect of each partial concentration was determined by analyzing the solution according to the methods already described. The character of the brines, their original composition, and the results of evaporation are given in the accompanying table. The changes in the concentration and the percentage loss of potassium as evaporation proceeded are also shown graphically in figures 24 and 25 (p. 70).

Changes resulting from the evaporation of artificial potash brines containing two acid radicles.

Character of solution.	Stages in the evaporation. ^a	Solution after evaporation.		Specific gravity.	Percentage composition of the solution.					Percentage loss.				K/Na ratio.
		Grams.	Per cent.		K.	Na.	Cl.	CO ₃ .	Total salts.	K.	Na.	Cl.	CO ₃ .	
KCl+Na ₂ CO ₃	A	500	100.0	2.10	6.94	1.90	9.06	20.00	0.30
	1	236	57.2	1.35	4.09	11.51	3.68	15.05	34.33	8.0	22	8.5	22	.36
	2	141	28.2	1.36	5.67	10.97	5.14	14.44	36.22	24	55	24	55	.52
	3	49	9.8	1.36	7.48	10.03	6.71	13.28	37.50	65	86	65	86	.73
K ₂ SO ₄ +Na ₂ CO ₃	A	500	100.0	1.80	6.94	2.20	9.06	20.0026
	1	192	38.4	1.39	3.06	13.00	3.12	17.33	36.51	35	28	46	27	.24
	2	58	11.6	1.38	3.68	12.30	2.56	17.17	35.71	76	79	87	78	.30
KCl+NaCl+Na ₂ SO ₄ ..	A	500	100.0	2.10	6.87	11.61	1.19	21.77	Cl	SO ₄	.31
	1	249	49.8	1.24	3.99	9.16	16.16	2.26	31.57	5.3	34	27	5.4	.44
	2	128	25.6	1.25	5.55	8.54	16.72	1.96	32.77	32	68	63	58	.65
	3	41	8.2	1.26	6.24	8.22	17.18	1.56	33.20	76	90	88	89	.76
KCl+NaCl+NaCO ₃ ..	A	500	100.0	2.10	8.03	11.61	2.26	24.00	CO ₃	.26
	1	277	55.4	1.26	3.55	10.06	14.72	3.43	31.76	6.4	31	30	16	.35
	2	117	23.4	1.29	5.51	9.77	14.02	5.18	34.48	39	72	72	46	.56
	3	60	12.0	5.39	10.50	12.30	7.47	35.66	69	84	87	60	.51
	4	40	8.0	5.10	11.12	11.22	8.98	36.42	81	89	92	68	.46
KCl+NaCl+Na ₂ B ₄ O ₇ ..	A	500	100.0	2.10	(?)	11.61	(?)	B ₄ O ₇
	1	166	33.2	5.14	8.88	17.29	1.08	31.89	19	(?)	51	(?)	.61
	2	95	19.0	6.21	8.00	17.41	1.60	33.22	44	7178
	3	38	7.6	6.11	8.15	17.10	2.28	33.64	78	8975

^a A=original solution.

The highest concentration of potassium, 7.48 per cent, was obtained with the solution containing potassium chloride and sodium carbonate and the lowest, 3.68 per cent, with that containing potassium sulphate and sodium carbonate. In the chloride-sulphate and chloride-borate brines the concentration of potassium increased to a little more than 6 per cent, but in the solution containing potassium chloride, sodium chloride, and sodium carbonate it increased to a maximum and then decreased. In general the contents of sulphate and sodium varied comparatively little after the first concentration. The chlorine concentration usually increased as evaporation progressed, but in the solution containing potassium chloride, sodium chloride, and sodium carbonate it decreased after the first concentration. In that solution the content of carbonate continually increased, but in the other carbonate brines it rapidly rose to a maximum and then slowly declined. The final mother liquor always contained a large amount of carbonate. The borate concentration steadily increased. The amount of dissolved salts increased in all the solutions to more than 33 per cent. The two solutions containing both chloride and carbonate yielded the strongest bitterns. The variations in the potassium-sodium ratio correspond closely to the changes in the concentration of the potassium. The highest ratio was reached in the chloride-borate solution, and the lowest in the sulphate-carbonate solution. The loss of potassium during the first concentrations was greatest in the sulphate-carbonate solution. The loss of potassium during the first concentrations was greatest in the sulphate-carbonate brine. In all the other solutions the loss was only 5 to 8 per cent while the solution was being concentrated to about half its original volume and the content of potassium was being doubled. During further evaporation the loss was very rapid in all the solutions. The steady increase in the percentage of total salts and the continual variations in the concentration of the constituents prove that equilibrium in the solutions did not reach final adjustment.

The variations in concentration of the potassium in the several solutions as evaporation proceeded are shown graphically in figure 24. The curve representing the solution containing potassium sulphate and sodium carbonate is practically a straight line whose moderate slope indicates that the concentration of the potassium is slow and the loss of it necessarily large.

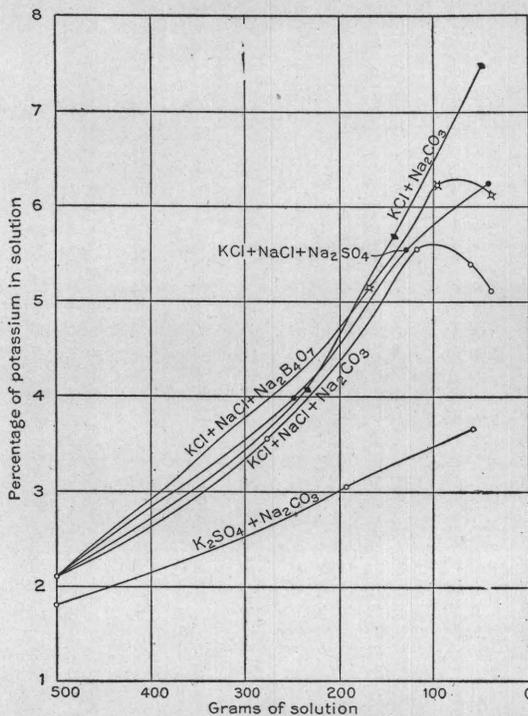


FIGURE 24.—Diagram showing the rate of concentration of potassium in various brines during evaporation.

in that containing potassium sulphate and sodium carbonate. With the exception of the curve for the latter solution the curves are all very much alike, sloping gently to a point corresponding to about half the quantity of the original solution and then becoming very steep. In other words, the loss of potassium sustained by the solutions during reduction to half their original volume and during concentration of the potassium to about 4 per cent is 5 to 8 per cent of that originally present, but during further evaporation the loss is very rapid.

ALKALI BRINES CONTAINING THREE ACID RADICLES.

More extensive evaporation experiments were carried out with solutions of the alkalis containing sulphate or borate in addition to chloride and carbonate. The character and composition of the brines used and the changes resulting through evaporation are given in the accompanying table. The change in concentration and the percentage loss of potassium for the sulphate solution is plotted in fig. 26 (p. 72).

The corresponding curves for the borate solution are so nearly identical with those given that they would unnecessarily confuse the diagram.

The curve representing the solution containing potassium sulphate and sodium carbonate is practically a straight line whose moderate slope indicates that the concentration of the potassium is slow and the loss of it necessarily large. The curves representing the concentration of potassium in the other solutions are similar to one another up to a concentration of about 5.5 per cent; beyond that point the curve for the solution of potassium chloride, sodium chloride, and sodium carbonate declines immediately and that of the borate reaches a maximum at 6.21 per cent.

Figure 25 gives a better idea of the losses of potassium sustained by the solutions than the table. From this it appears that at any particular stage in the evaporation the loss was least in the solution containing potassium chloride and sodium carbonate and greatest

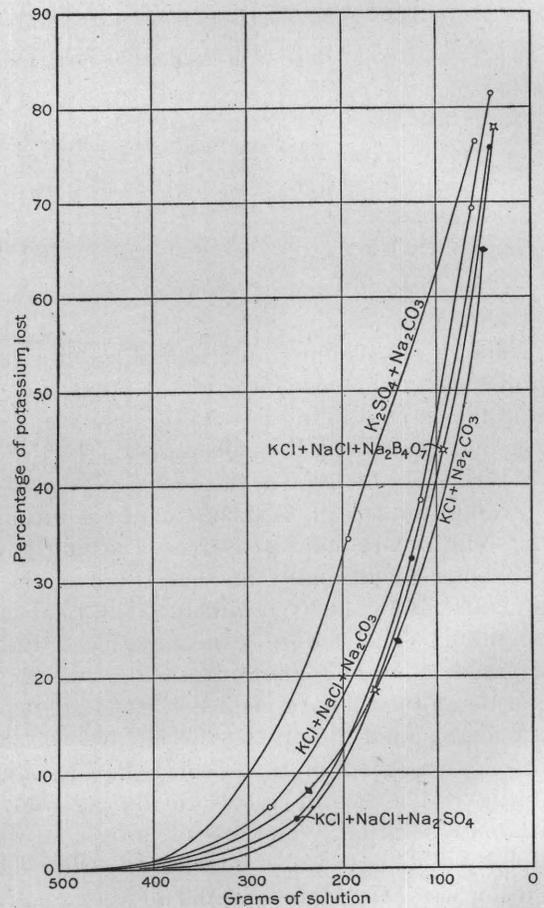


FIGURE 25.—Diagram showing the loss of potassium in various brines during evaporation.

Changes resulting from the evaporation of artificial potash brines containing three acid radicles.

Character of the solution.	Stages in the evaporation. ^a	Solution after evaporation (grams).	Specific gravity.	Percentage composition of the solution.						Potassium in total salts (per cent).	Percentage loss.					K/Na ratio.	
				K.	Na.	Cl.	CO ₃ .	SO ₄ .	Total salts.		K.	Na.	Cl.	CO ₃ .	SO ₄ .		
KCl+NaCl+Na ₂ CO ₃ +Na ₂ SO ₄ .	A	1,000	1.223	2.10	9.18	11.60	2.26	2.39	27.53	7.63	0.23
	1	723	1.268	2.86	10.64	13.53	2.68	3.05	32.76	8.73	1.6	16	16	14	7.527
	2	547	1.278	3.67	10.40	13.51	3.16	2.96	33.70	10.89	4.4	38	36	24	3235
	3	337	1.285	4.88	9.82	13.71	3.63	2.30	34.34	14.20	22	64	60	46	6750
	4	213	1.295	5.75	9.79	13.39	4.79	1.79	35.51	16.19	42	77	75	55	8459
	5	148	1.300	5.70	9.93	13.20	5.08	1.67	35.58	16.02	60	84	83	67	9057
	6	99	1.314	5.53	10.33	12.18	6.51	1.55	36.10	15.31	74	89	89	71	9354
	7	55	1.327	5.34	11.01	11.24	7.84	1.56	36.99	14.44	86	93	95	81	9649
8	22	1.335	5.28	11.26	10.86	8.36	1.59	37.35	14.14	94	97	98	92	9847	
KCl+NaCl+Na ₂ CO ₃ +Na ₂ B ₄ O ₇ .	A	1,000	1.238	2.10	(?)	11.60	2.27	B ₄ O ₇ (?)
	1	653	1.260	3.13	10.18	14.37	3.05	1.46	32.19	9.72	2.6	19	1231
	2	541	1.270	3.57	10.25	14.10	3.57	1.70	33.19	10.76	8	34	1535
	3	355	1.284	4.65	9.86	13.80	3.88	2.18	34.37	13.53	23	58	3947
	4	248	1.310	5.60	9.74	13.23	4.67	3.01	36.25	15.45	34	72	4957
	5	165	1.339	5.26	10.53	11.82	6.23	4.13	37.97	13.85	59	83	5550
	6	104	1.368	5.11	11.10	10.90	7.02	5.45	39.58	12.91	75	90	6846
	7	49	1.378	5.03	11.45	9.46	8.77	6.29	41.00	12.27	88	96	8144
8	17	1.388	4.82	11.80	9.42	8.63	6.39	41.06	11.74	96	98	9341	

^a A—original solution.

As evaporation progressed the potassium concentration of both solutions increased to about 6 per cent and then gradually decreased. The chlorine concentration rose to a maximum in each solution and then decreased. The carbonate concentrates increased rapidly in both brines, but finally showed a slight decrease in the borate solution. The borate concentration rose steadily to 6.39 per cent. The changes in the percentages of sulphate and sodium were slight. The quantity of dissolved salts in both solutions became greater as evaporation progressed. The final sulphate mother liquor contained 37.35 per cent of salts and that of the borate 41.06 per cent.

In the sulphate solution the potassium-sodium ratio increased from 0.23 to 0.59 and then decreased to 0.47. In the borate solution it reached a maximum of 0.57 and then decreased to 0.41.

The percentage of potassium lost from both solutions increased slowly until the brines had been reduced to about half their original volume. At this point the concentration of the potassium was about 4 per cent, and the loss amounted to 5 or 6 per cent of the potassium originally present. On further evaporation the loss was very rapid. At the maximum concentration of potassium only about one-fifth of the solution remained, and a loss of more than 35 per cent is recorded. By means of the curves in figure 26 the percentage loss corresponding to any concentration of potassium can be directly determined.

CONCLUSION.

According to the results set forth in this paper, the potassium is concentrated best in brines containing carbonates and chlorides, and poorest in those containing sulphates and carbonates, though a small amount of sulphate does not seem to hinder the concentration materially. In brines that contain several acid radicles the concentration of potassium may increase to a maximum as evaporation proceeds and then decline. The evidence at hand indicates that a large percentage of the potassium in a solution is lost during evaporation before the maximum con-

centration of potassium is attained. The loss is small until the potassium reaches a concentration of about 4 per cent, but it is very rapid during further evaporation. Therefore in the commercial extraction of potash from brines, especially those of the alkalis, it would seem

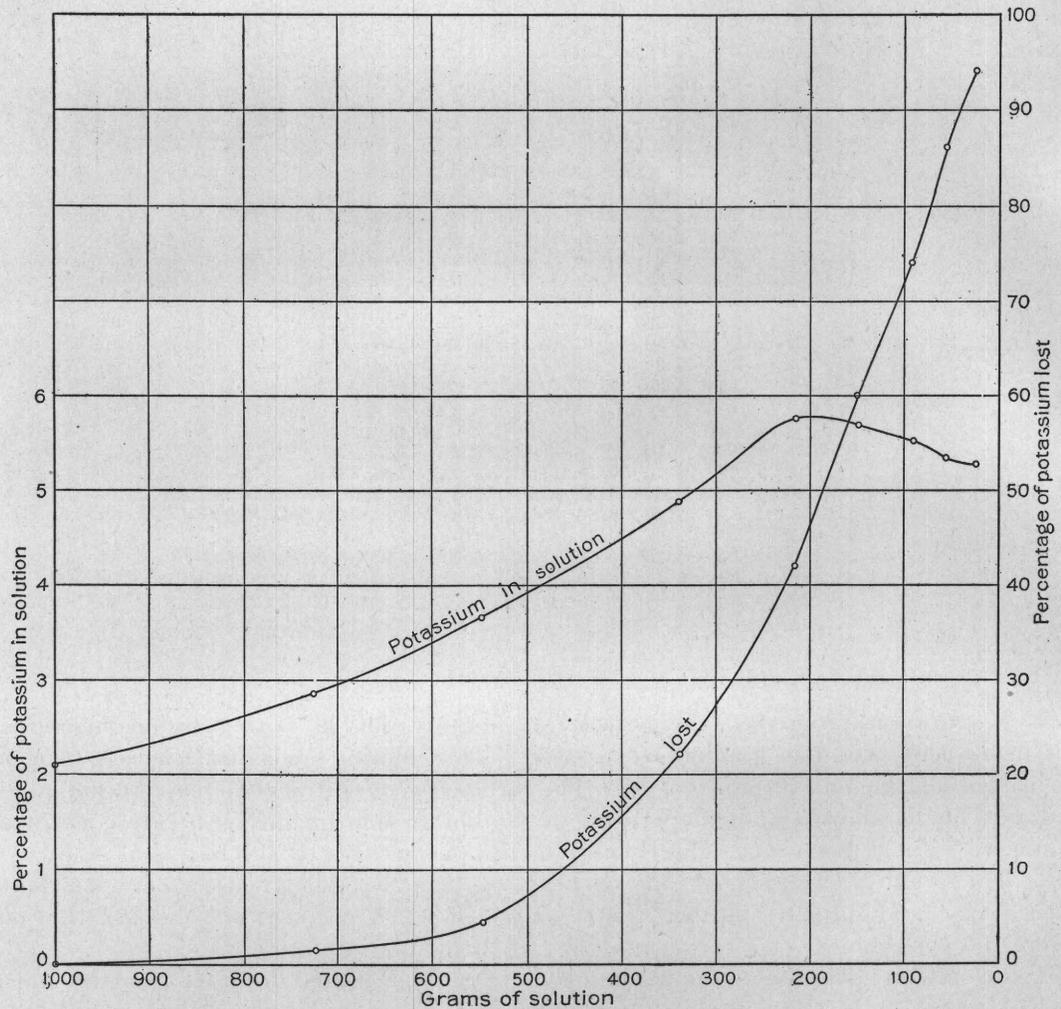


FIGURE 26.—Diagram showing the rate of concentration and the loss of potassium during the evaporation of a brine containing chlorides, carbonates, and sulphates of the alkalis.

best first to concentrate the solution by evaporation until it contained about 4 per cent of potassium, and then to subject the resulting bittern to other processes of manufacture. The most advantageous point of concentration would, however, have to be determined for each particular brine.