XXXI.—*Heterogeneous Equilibria between the Sulphates and Nitrates of Sodium and Potassium and their Aqueous Solutions. Part II. The Quaternary System* H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3.

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BEYOND the observations of some early investigators of the slow dissolution of potassium nitrate in saturated sodium sulphate solutions with the precipitation of sodium or potassium sulphate after a long time and of the ease with which sodium nitrate dissolves in solutions of potassium sulphate, no attempt seems ever to have been made to study the equilibria involved in the reciprocal salt transformation

$$Na_2SO_4 + 2KNO_3 \rightleftharpoons 2NaNO_3 + K_2SO_4.$$

The quaternary system formed by the addition of water to the two salt pairs, Na_2SO_4–KNO_3 and $NaNO_3$–K_2SO_4 presents certain features of interest and is of special importance in the determination of the most suitable conditions for the separation of the nitrates of sodium and potassium from the sulphates of these metals, with which they are found contaminated in nature in various parts of the world.*

The various binary and ternary systems which form the basis of the above quaternary system have been described in Part I (preceding paper). All the binary and ternary compounds which occur in the ternary systems occupy definite saturation surfaces in the quaternary system. In addition to these binary and ternary compounds at 25°, a compound occurs in the quaternary system, the composition of which it has not been found possible so far to determine. It occupies a definite saturation surface in the quaternary system, and further evidence on which the conclusion of its existence is based will be found in the following pages. The isotherm at 90° does not contain the saturation surface of this compound. There is therefore no doubt that it splits up at some temperature below 90° into its simple constituents.

Graphical Representation.—In order to represent graphically the experimental results, Schreinemakers's pyramidal method of representation (*Z. physikal. Chem.*, 1909, **69**, 557) has been used. Use has also been made of the various projection methods (*ibid.*, 1907,

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* See "Report on a Programme of Investigation for the Chilean Nitrate Industry," 1921, by Professor F. G. Donnan; the Report of the Indian Industrial Commission, 1916–18, Appendix F; and a Report on the Manufacture and Composition of Indian Saltpetre by Hooper (Agricultural Ledger, No. 3, 1905).

TABLE I.

The System H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3 *at* 25°.

Point.	Composition in molar percentages.				Solid phases.
	Na_2SO_4.	$Na_2(NO_3)_2$.	K_2SO_4.	$K_2(NO_3)_2$.	
a	3·42	—	—	—	$Na_2SO_4,10H_2O$
	2·85	1·02	—	—	,,
b	3·05	3·80	—	—	$Na_2SO_4,10H_2O + Na_2SO_4$
l	3·35	—	0·96	—	$Na_2SO_4,10H_2O + D_2$
m	2·89	2·75	0·74	—	$Na_2SO_4,10H_2O + Na_2SO_4 + D_2$
	3·01	3·92	—	—	Na_2SO_4
c	2·78	4·27	—	—	$Na_2SO_4 + D_1$
	2·76	4·44	0·67	—	,,
n	2·66	4·49	1·27	—	$Na_2SO_4 + D_1 + D_2$
	2·34	4·70	—	—	D_1
	1·82	5·51	—	—	,,
	1·15	7·04	—	—	,,
e	0·68	8·63	—	—	$D_1 + NaNO_3$
	0·74	8·47	—	0·23	,,
r	1·05	7·91	—	0·60	$D_1 + NaNO_3 + T$
f	—	8·81	—	—	$NaNO_3$
	—	8·97	—	0·40	,,
	—	9·03	—	0·80	,,
	—	9·10	—	1·59	,,
	—	9·18	—	2·36	,,
g	—	9·31	—	3·58	$NaNO_3 + KNO_3$
	1·17	8·36	—	1·69	$NaNO_3 + T$
	0·77	8·97	—	3·20	,,
s	0·67	9·10	—	3·63	$NaNO_3 + KNO_3 + T$
	—	5·78	—	3·39	KNO_3
	—	3·94	—	3·26	,,
	—	2·01	—	3·17	,,
	—	1·52	—	3·18	,,
	—	1·02	—	3·20	,,
	—	0·51	—	3·26	,,
h	—	—	—	3·34	,,
	—	—	0·28	3·11	,,
i	—	—	0·62	2·89	$KNO_3 + K_2SO_4$
	—	—	0·85	1·18	K_2SO_4
	—	—	1·04	0·49	,,
j	—	—	1·23	—	,,
k	0·83	—	1·34	—	$K_2SO_4 + D_2$
	1·18	—	1·09	0·44	,,
	1·09	—	0·89	0·69	,,
	0·99	—	0·32	1·75	,,
v	—	1·16	0·92	2·70	$K_2SO_4 + D_2 + KNO_3$
	—	2·12	0·99	2·32	$D_2 + KNO_3$
	—	4·91	1·33	1·82	,,
q	—	7·91	1·61	1·65	$D_2 + KNO_3 + T$
	—	8·47	0·96	2·32	$KNO_3 + T$
	1·63	5·42	1·60	—	$D_1 + D_2$
	1·08	6·35	1·92	—	,,
	0·75	7·13	2·09	—	,,
	0·13	8·32	2·30	—	,,
p	—	9·13	2·27	0·41	$D_1 + D_2 + T$
	—	8·82	1·90	0·84	$D_2 + T$

$D_1 = Na_2SO_4,NaNO_3,H_2O$. $D_2 = K_3Na(SO_4)_2$. T = ?.

59, 663) for the confirmation of solid phases by the " rest method " in certain parts of the system. It may be pointed out that by the term, orthogonal projection, is meant a projection made on to the ground plane by means of parallel lines perpendicular to the base of the pyramid.

The experimental and analytical methods used were the same as described in Part I. The data for the system H_2O–$NaNO_3$–KNO_3 at 25° are taken from Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 106).

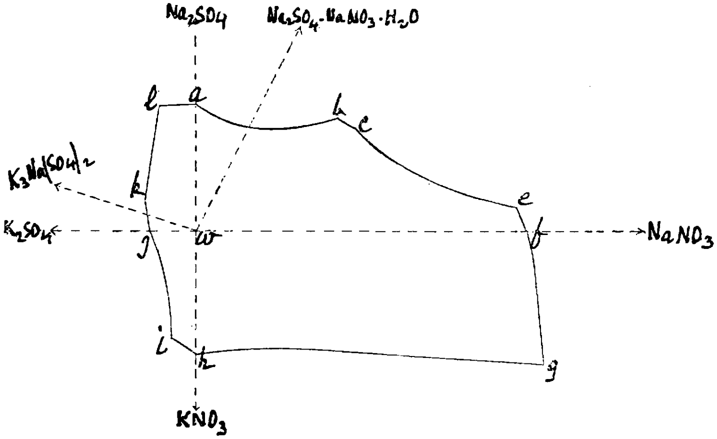
The Isotherm at 25°.—The compositions of the binary, ternary and quaternary solutions saturated at this temperature are expressed in g.-mols. of the various salts per 100 g. of the solution in Table I. The molecular formulæ of sodium and potassium nitrates have been doubled in order to give them equal replacing powers with sodium and potassium sulphates.

The Orthogonal Projection.—For the further discussion of the system, we shall use the orthogonal projection which is shown in Figs. 1 and 2. The apex, W, of the pyramid which represents pure water projects to the point *w* in these figures. The four ternary isotherms which form the boundary of the quaternary isotherm are shown in this projection separately in Fig. 1. As has been pointed out in Part I, the point *l* represents a ternary isothermal invariant solution which is in equilibrium not with Glauber's salt and glaserite, but with Glauber's salt and a solid solution of glaserite and sodium sulphate of the composition $K_2SO_4 = 78{\cdot}6\%$, $Na_2SO_4 = 21{\cdot}4\%$. This introduces no new complication in the quaternary system provided there is always an excess of sodium sulphate present in the solid phase to form the solid solution of glaserite and sodium sulphate of the above composition. Strictly speaking, therefore, where glaserite is mentioned as a solid phase along with sodium sulphate, its composition is given by the above value. The difference between the composition of glaserite and that of its solid solution is not, however, very large and for all practical purposes glaserite may be assumed to be of the constant composition $K_3Na(SO_4)_2$. It may be seen that the line joining the point representing the composition of pure glaserite to the origin (apex in the space model) cuts the saturation curve of potassium sulphate and not that of glaserite. Glaserite is therefore decomposed by water and the ternary invariant solution *l* is incongruently saturated.

In order to show the positions of the quaternary saturation surfaces of Glauber's salt and sodium sulphate and the quaternary isothermal invariant point *m* more clearly in the projection, the ternary saturation curve *ab* of Glauber's salt in the system H_2O–Na_2SO_4–$NaNO_3$ is drawn as a straight line in Fig. 2, although the actual form of the curve is that shown in Fig. 1.

The darapskite field is enclosed by the curves *ce*, *er*, *rp*, *pn*, and *cn*. Here again the line joining the point representing the composition of pure darapskite to the origin passes through the Glauber's salt and glaserite fields and not through that of darapskite. Darapskite also is therefore decomposed by water.

FIG. 1.



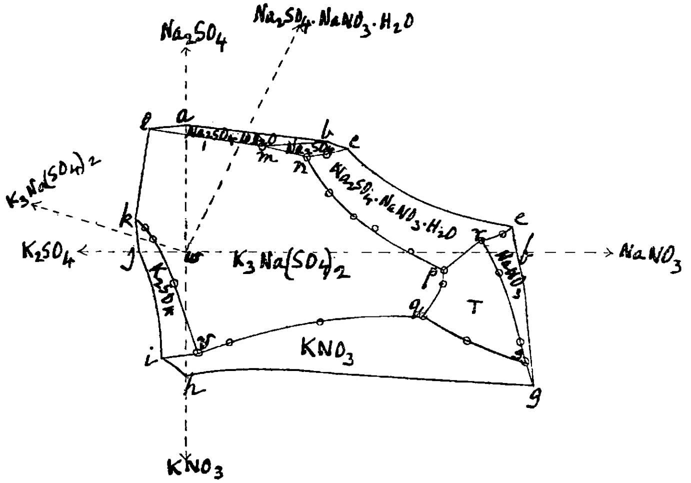


FIG. 2.

The quaternary saturation curves *er*, *rs*, and *sg* mark the inner boundary limit of the sodium nitrate field. The composition of the solution containing the maximum amount of potassium nitrate, which the ternary invariant solution *e* in contact with darapskite and sodium nitrate can dissolve, is given by the point *s*. The same quaternary solution *s* is obtained when an excess of either sodium or potassium sulphate is added to the ternary invariant solution *g* in contact with excess of solid sodium and potassium nitrates.

The point *v* (Fig. 2) represents a quaternary invariant solution in equilibrium with three solid phases, potassium sulphate, glaserite and potassium nitrate. The composition of this solution, as will be seen from the position of the point *v* in Fig. 2, cannot be represented in terms of the solid phases with which it is in equilibrium. This solution is therefore incongruently saturated.

On the addition of sodium nitrate to the solution *v* in contact with glaserite, potassium sulphate and potassium nitrate, the following reaction occurs :

$$NaNO_3 + 2K_2SO_4 = K_3Na(SO_4)_2 + KNO_3.$$

This reaction does not affect the composition of the quaternary invariant solution *v*, so long as there is any solid potassium sulphate present in contact with the solution. When so much of the sodium nitrate has been added that the whole of the solid potassium sulphate which was present in contact with the solution *v* is converted into glaserite and potassium nitrate, it disappears as a solid phase and the system acquires a degree of freedom. The point representing the compositions of the monovariant quaternary solutions then traverses the curve *vq* on the additions of increasing quantities of sodium nitrate to the solution *v*. The two solid phases in equilibrium with all quaternary solutions, the compositions of which are represented by points on the curve *vq* between the points *v* and *q*, are glaserite and potassium nitrate. When so much of the sodium nitrate has been added that the composition of the quaternary solution is represented by the point *q*, a distinct halt occurs in the movement of the point representing the compositions of the quaternary solutions, and further additions of sodium nitrate do not change the composition of the solution *q*, so long as there is sufficient glaserite present in contact with it. It is the persistence of the constant composition of the solution at *q* in contact with solid glaserite and potassium nitrate with increasingly small additions of sodium nitrate that leaves no doubt as to *q* being an invariant point.

The above facts combined with the positions of the curves *np* and *pq* all point to the existence of a new solid phase in the quaternary system. Before describing the various attempts that have been made to determine the nature of this new solid phase, we shall sum up briefly the meanings of the various curves and surfaces in the quaternary isotherm at 25°. The letter T stands for the new solid phase.

almb	is the saturation field of	Glauber's salt.
bcnm	,, ,, ,,	sodium sulphate.
cnpre	,, ,, ,,	darapskite.
efgsr	,, ,, ,,	sodium nitrate.
rpqs	,, ,, ,,	T
gsqvih	,, ,, ,,	potassium nitrate.
kjiv	,, ,, ,,	potassium sulphate.
klmnpqv	,, ,, ,,	glaserite and solid solutions of glaserite and sodium sulphate.

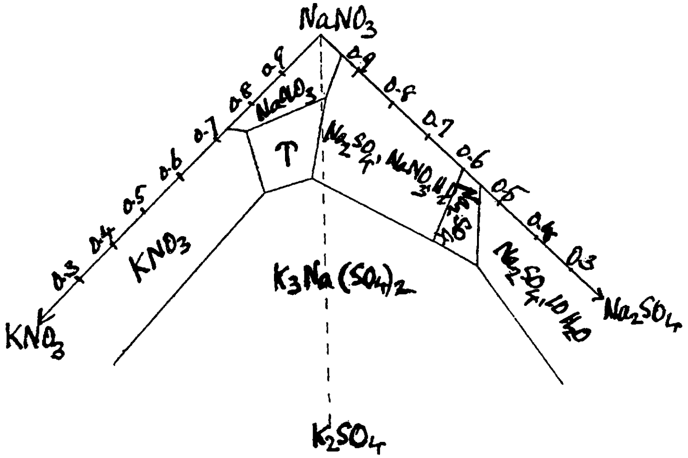
Quaternary curves :

bm	is the saturation curve of	Glauber's salt and sodium sulphate.
lm	,, ,, ,,	Glauber's salt and glaserite.
mn	,, ,, ,,	sodium sulphate and glaserite.
cn	,, ,, ,,	sodium sulphate and darapskite.
np	,, ,, ,,	darapskite and glaserite.
er	,, ,, ,,	darapskite and sodium nitrate.
rp	,, ,, ,,	darapskite and the compound T.
rs	,, ,, ,,	sodium nitrate and the compound T.
gs	,, ,, ,,	sodium nitrate and potassium nitrate.
sq	,, ,, ,,	potassium nitrate and the compound T.
pq	,, ,, ,,	glaserite and the compound T.
qv	,, ,, ,,	glaserite and potassium nitrate.
iv	,, ,, ,,	potassium sulphate and potassium nitrate.
kv	,, ,, ,,	potassium sulphate and glaserite.

The saturation curves and surfaces intersect in points representing solutions which are saturated with three solids. These quaternary invariant points are *m*, *n*, *p*, *q*, *r*, *s*, and *v*. The actual compositions of these solutions as well as the solids with which they are in equilibrium will be found in Table I.

The Nature of the Phase T.—The improbability of the existence of any compound other than darapskite of sodium sulphate and sodium nitrate has been pointed out in Part I. The positions of the various quaternary invariant points and those of the quaternary saturation curves and the existence of the enclosed area *rpqs* in Fig. 2 point clearly to the formation of a definite compound in the quaternary system. That this is essentially a quaternary compound, a triple or a tetragenic double salt, is indisputable. Attempts to isolate it by the evaporation of unsaturated solutions have proved fruitless. It will be seen by reference to Fig. 2 that points in the area *rpqs* represent solutions which are saturated with one solid only, *viz.*, the compound T. The points representing the compositions of unsaturated solutions which will deposit this compound on isothermal evaporation as the first solid also project on to this area in the orthogonal projection. The compositions of all such unsaturated solutions which will deposit T as the first solid on evaporation cannot be read directly from this projection. Jänecke's method of representation (" Gessättigte Salzlösungen ") is of inestimable value for this purpose. A part of the Jänecke diagram is shown in Fig. 3. The proportions of dry salts contained by an unsaturated solution which will deposit T as the first solid on evaporation can be read from this figure at a glance. To hasten the process of evaporation, such mixtures of dry salts were dissolved in excess of water and the unsaturated solutions evaporated at higher temperatures to such an extent that when cooled to 25° they were expected to deposit T as the first solid. This method of procedure unfortunately suffers from the serious defect that the solubility of sodium sulphate in solutions of potassium and sodium nitrates decreases with rise of temperature and consequently sodium sulphate is deposited at higher temperatures from solutions which are not saturated at 25° with respect to this salt. This fact makes it very difficult to adjust the whole course of evaporation in such a way that when the hot solution is cooled to 25° it should deposit T. Actually all such attempts have resulted in solutions, the compositions of which lie very near to the point *s* (Fig. 2), which is undoubtedly the crystallisation end-point of the system. In the isothermal evaporation at 25°, the solution remains supersaturated for a considerably long time. In all these cases of evaporation it has been found that crystallisation starts after the process of evaporation has been carried too far. This tendency to form supersaturated solutions has been noticed by van 't Hoff in many cases, particularly those of kieserite, leonite and kainite ($MgSO_4$,KCl,$3H_2O$) (" Zur Bildung der Ozeanischen Salzablagerungen," 1905, **1**, 28). The present case seems analogous to these and requires similar handling which

FIG. 3.



necessitates the measurements of the vapour pressure of the hydrated double salt, darapskite, as well as those of the saturated solutions at this temperature (*op. cit.*).

The Isotherm at 90°.—The isotherm at 90° is not so complicated as that at 25°. The only double salt that occurs in the system at this temperature is glaserite. All others seem to break down at temperatures below 90°. In the ternary systems, only the invariant points have been determined, and although the ternary curves have not been followed completely, it is probable that in most cases they are not very different from straight lines. Furthermore, as the quaternary curve l_1x is practically a straight line, there is no doubt that the hydrated double salt, darapskite, in the ternary system H_2O–Na_2SO_4–$NaNO_3$ and the compound T in the quaternary system split up into the simple salts at temperatures lower than 90°. The isotherm is shown in Fig. 4 as the orthogonal projection of the space model, and the data for the system at this temperature are in Table II in terms of molar percentages.

FIG. 4.

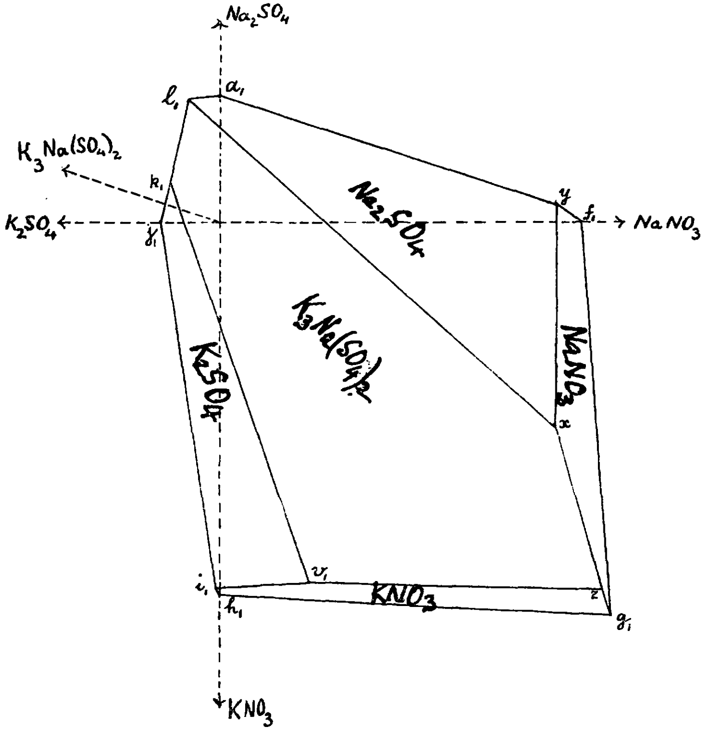


TABLE II.

The System H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3 *at* 90°.

Point.	Composition in molar percentages.				Solid phases.
	Na_2SO_4.	$Na_2(NO_3)_2$.	K_2SO_4.	$K_2(NO_3)_2$.	
a_1	5·13	—	—	—	Na_2SO_4
l_1	4·98	—	1·25	—	$Na_2SO_4 + D_2$
	1·39	4·72	2·19	—	,,
	—	6·65	2·04	0·41	,,
x	—	14·29	0·64	8·34	$Na_2SO_4 + D_2 + NaNO_3$
y	0·71	13·72	—	—	$Na_2SO_4 + NaNO_3$
f_1	—	14·67	—	—	$NaNO_3$
g_1	—	15·81	—	16·02	$NaNO_3 + KNO_3$
z	—	16·20	0·70	14·96	$NaNO_3 + KNO_3 + D_2$
	—	12·17	0·67	14·78	$KNO_3 + D_2$
h_1	—	—	—	15·26	KNO_3
i_1	—	—	0·16	14·89	$KNO_3 + K_2SO_4$
j_1	—	—	2·37	—	K_2SO_4
k_1	1·49	—	1·97	—	$K_2SO_4 + D_2$
v_1	—	4·16	0·59	14·78	$K_2SO_4 + D_2 + KNO_3$

$D_2 = K_3Na(SO_4)_2$.

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