Mechanism of the Reaction.—A plausible mechanism to fit the data, especially in the case of excess water is

$$B_2H_6 \rightleftarrows 2BH_3 \qquad (13)$$

$$BH_3 + H_2O \longrightarrow [BH_3 \cdot H_2O]^* \longrightarrow BH_2OH + H_2 \qquad (14)$$

$$BH_2OH + H_2O \longrightarrow [BH_2OH \cdot H_2O]^* \longrightarrow BH(OH)_2 + H_2 \qquad (15)$$

$$BH(OH)_2 + H_2O \longrightarrow [BH(OH)_2 \cdot H_2O]^* \longrightarrow B(OH)_3 + H_2 \qquad (16)$$

In the case of excess diborane it may be possible for borine to react with the intermediates to give rise to other boric acid products, *e.g.*, metaboric acid. Because of the relatively low concentrations of the partially hydrolyzed intermediates it is unlikely that any disproportionation reaction occurs in the mechanism.

Intermediate Products of the Reaction.—The mechanism postulated for the hydrolysis of diborane involves various intermediates which could not be isolated in the vapor phase reaction. Evidence of the existence of these intermediates has been obtained from the reaction of diborane with ice and with the "bound water" in silica gel.[10]

Diborane reacts with ice at −80° to give a 4:1 ratio of hydrogen to diborane consumed. This reaction presumably is a surface reaction in which each boron atom is attached to two hydroxyl groups in the surface of the ice crystal. An active hydrogen atom remains attached to each boron atom. At −23° there evidently is sufficient mobility of the molecules within the ice crystal to permit this active hydrogen atom to react. The final hydrogen to diborane ratio approaches 6:1. It appears that these experiments give the closest approach to direct evidence for the formation of a $BH(OH)_2$ molecule.

When diborane is exposed to the "bound" water in silica gel (the gel being heated previously to 150° to ensure complete removal of adsorbed water) at a low temperature (−23°), hydrolysis occurs with the hydrogen to diborane consumed ratio being *ca.* 2:1.[10] The state of hydrolysis at this point corresponds to the formation of BH_2OSi– which is analogous to the formation of BH_2OH (eq. 14). In the case of silica gel, however, the silicon atoms serve as anchor points to prevent the migration of the partially hydrolyzed borine and, consequently, limit its degree of hydrolysis.[10]

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PASADENA, CALIF.

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[10] I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Aqueous Solubility Relations of Potassium Molybdate, and Aqueous Ternary Isotherms at 25° with KOH, KNO_3 and KIO_3

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The system K_2MoO_4–H_2O, with a eutectic at −38° and a boiling point of 119° for the saturated solution, involves anhydrous K_2MoO_4 throughout. Over the range directly studied, −18° to 119°, the solubility of the salt, in weight percentage, varies very little and practically linearly with the temperature: $S = 63.82 + 0.0300t$. The anhydrous nature of the solid phase was further confirmed through solubility measurements in presence of KOH. The ternary systems with KNO_3 and with KIO_3, studied at 25°, involve only the separate salts as solid phases.

Despite Amadori's work[1] on the ternary systems K_2MoO_4–K_2SO_4–H_2O and K_2MoO_4–K_2CrO_4–H_2O, involving continuous solid solutions of the salts, and in which the salt K_2MoO_4 appeared definitely to be anhydrous as the saturating phase at room temperature, there seemed still to be some uncertainty regarding the hydration of this salt. The uncertainty may have continued because of old reports of various improbable hydrates cited in Gmelin and in Mellor; and the formula $K_2MoO_4 \cdot 5H_2O$ is still listed in a current handbook. In fact, commercially supplied C.P. potassium molybdate was received with the label of a pentahydrate in 1950, although the contents of the various 5-lb. bottles was strictly anhydrous. The binary system K_2MoO_4–H_2O was therefore investigated over a wide range and further information was sought through the study of the ternary system K_2MoO_4–KOH–H_2O at 25°. The systems K_2MoO_4–KNO_3–H_2O and K_2MoO_4–KIO_3–H_2O were also investigated at 25°, for comparison with the corresponding systems involving the sodium salts.[2,3] In all the work no hydrate of K_2MoO_4 was observed.

The general experimental procedure of equilibration, sampling, analysis, proof of equilibrium, etc., used for the solubility determinations, both binary and ternary, was the same as that used in the investigation of similar systems involving Na_2MoO_4[2,3] and $MgMoO_4$.[4] The K_2MoO_4 used was about 99.9% pure, on the basis of the volumetric determination of molybdate with standard $AgNO_3$ and standard KCNS, in an adaptation of the Volhard method.[2] One batch of the salt was found to form a slight white deposit from moderately concentrated solutions, and was therefore recrystallized before analysis and use.

System K_2MoO_4–H_2O.—The solubility curve from 9 to 90° was determined by direct analysis of the filtered solution, in some cases by evaporation

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[1] M. Amadori, *Atti R. accad. Lincei*, [5] **21**, I, 667 (1912).

[2] For Na_2MoO_4–$NaNO_3$–H_2O: J. E. Ricci and L. Doppelt, THIS JOURNAL, **66**, 1985 (1944).

[3] For Na_2MoO_4–$NaIO_3$–H_2O: J. E. Ricci and W. F. Linke, *ibid.*, **69**, 1080 (1947).

[4] J. E. Ricci and W. F. Linke, *ibid.*, **73**, 3603 (1951).

to dryness at 100° with final heating at ~300°, in some cases by the volumetric determination of molybdate (Volhard method), and in a few cases by both methods. The results listed in Table I are averages of closely agreeing duplicate measurements. The solid phase, dried in the open air at room temperature, was found to be anhydrous. (In warm, damp weather it is slightly deliquescent.) The solid is evidently anhydrous throughout since the solubility curve is quite smooth. The actual points fall, in fact, upon a straight line, with wt. % K_2MoO_4 = 63.82 + 0.0300 $t°$, the average absolute deviation, determined by means of least squares, being 0.069% K_2MoO_4, or ~1.1 part per thousand. A direct determination of the solubility at −18.1° gave 63.15% (average of 63.02 and 63.27), as compared to the value 63.28% expected by linear extrapolation. The values for the boiling point were determined by boiling a quantity of unsaturated solution containing a known weight of the salt to the point of visible crystallization, whereupon the composition was calculated from the residual total weight of the solution (~150 g.), and also by direct analysis after rapid filtration of a boiling saturated solution. The two observations gave temperatures between 118.5 and 119.5° as the boiling point and values from 67.22 to 67.96% as the solubility. The average, 67.60%, is close to the value 67.39% given by linear extrapolation to 119° of the solubility curve determined up to 90°.

TABLE I

SYSTEM K_2MoO_4–H_2O

Temp., °C.	Wt. % K_2MoO_4	Temp., °C.	Wt. % K_2MoO_4
Ice + soln. + vapor		K_2MoO_4 + soln. + vapor	
−2.1	11.00	27.59	64.59
−4.7	19.81	31.40	64.80
−7.1	26.83	34.91	64.78
−15.6	40.24	40.41	65.03
−16.7	41.72	46.23	65.07
−22.5	46.88	52.88	65.30
		56.89	65.41
Ice + K_2MoO_4 +		59.15	65.61
soln. + vapor		64.46	65.72
−38	62.7	70.01	65.98
K_2MoO_4 + soln. + vapor		76.65	66.19
−18.1	63.15	81.93	66.39
+ 9.00	64.22	89.96	66.54
17.94	64.46	Boiling point, satd.	
25.00	64.57	119	67.6

The salt potassium molybdate, therefore, is distinguished by having a high solubility, changing very little with temperature (only 2.4 out of 65% in 80°), and with a practically linear change throughout. The 25° solubility reported by Amadori[1] was 64.86%, to be compared with the value 64.57% here found. The density of the saturated solution was measured at two temperatures: 1.803 at 9° and 1.800 at 25°.

The ice curve was determined by means of cooling curves on unsaturated solutions of known composition. Difficulties caused by supercooling and by solidification interfering with adequate stirring prevented determinations below −22.5°. A constant temperature of ~ −36.5° was observed, however, for all the mixtures, including others expected to freeze below −22.5°. Since this temperature agrees fairly well with the extrapolated intersection (−39°) of ice curve and solubility curve (for K_2MoO_4), the probability is that the solid phase for the salt remains anhydrous down to the eutectic, at ~ −38° and ~62.7% K_2MoO_4 (Fig. 1).

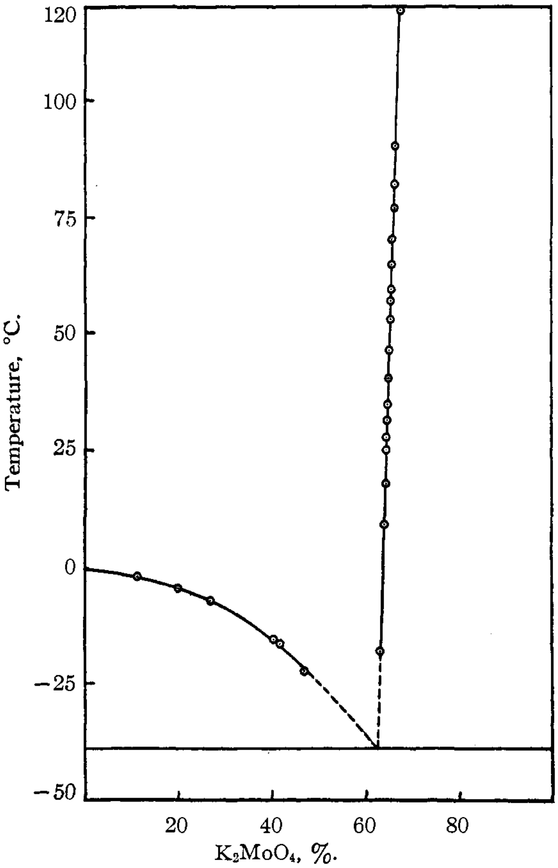

Fig. 1.—System K_2MoO_4–H_2O.

Part of the System K_2MoO_4–KOH–H_2O at 25°.—Since the direct analysis of the solid phase in the system K_2MoO_4–H_2O involves uncertainty in the possible decomposition of some low hydrate before analysis, a part of the 25° isotherm of the ternary system with KOH was studied in order to verify the anhydrous nature of the saturating salt. KOH was chosen for this purpose for three reasons: its high solubility would give a long isothermal solubility curve for the molybdate, its concentration in the solution could be determined directly and accurately, and it would not be expected to form either compounds or solid solution with the salt being studied. Carbonate-free aq. KOH (~40% by weight) was prepared by treatment with excess of pure $Ba(OH)_2$. The exact concentration of the solution was determined by titration with standard (1 *N*) H_2SO_4, and weighed amounts of it, together with weighed amounts of K_2MoO_4 and water, were used to prepare complexes of known composition. The saturated ternary solution was then analyzed for each of the two solutes. KOH was determined by titration with 1 *N* H_2SO_4 to the brom thymol blue end-point, after it had been shown that a considerable concentration of K_2MoO_4 did not interfere.[5] The neutralized solution was then used for the volumetric determination of molybdate. The data are listed in Table II and plotted in Fig. 2.

TABLE II

PART OF SYSTEM K_2MoO_4–KOH–H_2O AT 25°; SATURATION WITH K_2MoO_4

Complex K_2-MoO_4, %	Complex KOH, %	Saturated solution K_2MoO_4, %	Saturated solution KOH, %	Extrapolation error % KOH at 100% K_2MoO_4
72.29	1.71	60.94	2.29	+0.29
66.80	4.08	56.91	5.27	+ .09
55.04	11.15	43.04	13.93	+ .73
46.46	17.41	31.17	22.28	+ .36
39.19	20.45	28.47	23.88	+ .99
23.86	30.53	16.00	33.51	+1.66

From the compositions of total complex and saturated solution, the hydration of the solid phase was determined by algebraic extrapolation of tie-lines.[6] Within the probable experimental uncertainty of the measurements, the solid phase was found to be anhydrous K_2MoO_4 throughout. When extrapolated to the line of 100% K_2MoO_4, the six tie-lines gave an average deviation of 0.7, in terms of % KOH, from the corner of the diagram representing pure K_2MoO_4. The individual deviations are listed in the last column of Table II. The first four are much more significant than the last two, in which the extrapolation multiplies the experimental errors about eight times. The isotherm was not continued to higher KOH concentrations because it would require carbonate-free solid KOH; nevertheless, some rough experiments with the available carbonate-free 40% KOH solution and some solid in addition showed that the isothermally invariant solution for saturation with both solutes is very close (within ~1%) to the solubility of KOH alone, or point a of Fig. 2.

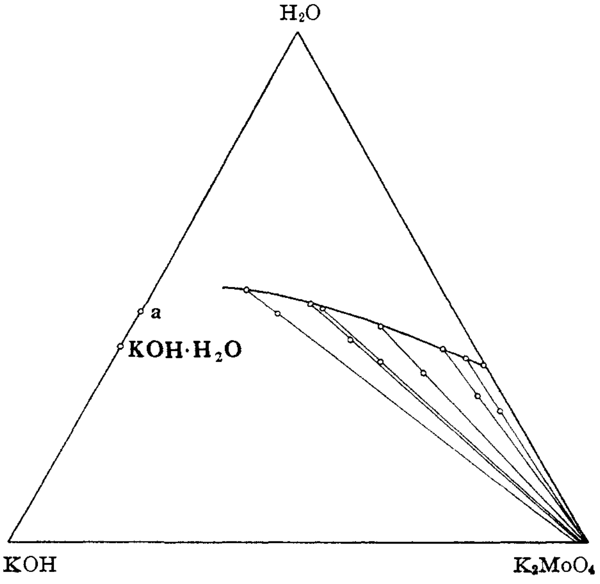

Fig. 2.—Part of the system K_2MoO_4–KOH–H_2O at 25°.

System K_2MoO_4–KNO_3–H_2O **at 25°.**—The saturated solution in this system was analyzed by evaporation to dryness for total solid, and by volumetric determination of molybdate for percentage of K_2MoO_4. Graphical and algebraic consideration of the data, listed in Table III, shows the only solids involved to be the separate, pure anhydrous salts.

TABLE III

SYSTEMS H_2O–K_2MoO_4(A)–KNO_3(OR KIO)$_3$(B), AT 25°

Complex % A	Complex % B	Saturated solution % A	Saturated solution % B	Saturated solution density	Solid phase
...	0.00	64.57	0.00	1.800	K_2MoO_4
69.15	2.64	63.08	3.14	1.821	K_2MoO_4
69.71	3.00	62.67	3.80	1.827	K_2MoO_4
69.02	3.53	62.49	4.30	1.831	K_2MoO_4
68.76	4.03	61.98	5.17		K_2MoO_4
64.25	5.98	62.03	5.30	1.843	K_2MoO_4 + KNO_3
58.03	12.92	62.15	5.22	1.843	K_2MoO_4 + KNO_3
52.12	26.13	62.01	5.25		K_2MoO_4 + KNO_3
Average		62.06	5.26	1.843	K_2MoO_4 + KNO_3
53.04	18.02	61.28	5.19	1.827	KNO_3
48.85	20.03	57.91	5.08	1.753	KNO_3
36.62	25.46	46.08	6.23	1.565	KNO_3
28.82	26.30	35.43	9.35	1.433	KNO_3
20.08	31.27	25.32	13.25	1.353	KNO_3
11.04	37.63	14.39	18.65	1.270	KNO_3
0.00	...	0.00	27.71	1.193	KNO_3
70.06	3.38	63.94	1.15	1.822	K_2MoO_4 + KIO_3
66.99	8.09	63.97	1.15	1.823	K_2MoO_4 + KIO_3
60.76	14.67	63.93	1.20	1.818	K_2MoO_4 + KIO_2
Average		63.95	1.17	1.821	K_2MoO_4 + KIO_3
47.25	22.85	60.52	1.13		KIO_3
43.00	24.87	56.57	1.13	1.683	KIO_3
37.08	28.38	51.08	1.30	1.600	KIO_3
32.47	27.25	43.86	1.63	1.484	KIO_3
28.12	27.59	38.10	1.92	1.406	KIO_3
22.63	28.63	30.97	2.33	1.331	KIO_3
15.97	28.74	21.75	2.92	1.225	KIO_3
11.09	23.24	13.93	3.69	1.151	KIO_3
7.36	29.45	10.00	4.37	1.115	KIO_3
0.00	...	0.00	8.45	1.071	KIO_3

System K_2MoO_4–KIO_3–H_2O **at 25°.**—In this system the analysis involved determination of total solid by evaporation and iodometric determination of iodate by treatment with iodide and acid and titration with thiosulfate. This titration of iodate in presence of molybdate requires careful control of the quantity of acid used, since a certain amount of acid is consumed in the formation of polymolybdate ions, and since, at the same time, high acidity causes the molybdate itself to liberate iodine. The conditions used were those already worked out for the corresponding system of the sodium salts.[3] The results, listed in the lower part of Table III, show, as in the preceding system, that the only solids are the pure, anhydrous salts.

As in the corresponding systems Na_2MoO_4–$NaNO_3$–H_2O[2] and Na_2MoO_4–$NaIO_3$–H_2O,[3] therefore, no double compounds are formed at this temperature. An unusual compound of the formula $K_2O \cdot I_2O_5 \cdot 2MoO_3 \cdot H_2O$ is mentioned by Sidgwick,[7] but evidently such a compound, if it exists, is to be looked for in the quaternary system KOH–I_2O_5–MoO_3–H_2O.

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(5) A similar procedure was used by J. Byé for the system NaOH–MoO_3–H_2O; *Bull. soc. chim.*, **10**, 239 (1943).

(6) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

(7) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford Univ. Press, 1950, p. 1042.