valence electrons without disturbing the electronic balance of the atom from which it separates.

Summary

There seem to be at least three types of oxidation reactions.

1. Oxidation by the transfer of an electron from one atom to another.

2. Addition of a positive hydroxyl group, $\mathrm{H}:\overset{..}{\underset{..}{\mathrm{O}}}{}^{+}$, to an unshared pair of electrons, either of a negative ion or of an electrically neutral molecule. In the latter case a hydrogen ion separates and a semipolar union is formed.

3. Separation of a semipolar oxygen atom in an electrically neutral condition followed by its union with an unshared pair of electrons. The oxygen atom may either remain in the semipolar condition in the new compound or may take up a hydrogen ion and form an hydroxyl group.

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

TERNARY SYSTEMS. VIII. POTASSIUM CARBONATE, POTASSIUM SULFATE AND WATER AT 25°

BY ARTHUR E. HILL AND SAMUEL MOSKOWITZ

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The solubilities of potassium carbonate and potassium sulfate in water have been studied by Blasdale[1] and more recently by de Ropp,[2] in both cases as part of a study of a four-component system. The two papers give data for the solubilities, however, at the isothermally invariant points only; the solubilities at intermediate concentrations having been determined in this Laboratory, the results are communicated to complete the picture.

Anhydrous potassium carbonate (Kahlbaum's "zur Analyse") and potassium sulfate (purified by recrystallization) were taken in weighed amounts and agitated with measured amounts of water at 25 ± 0.05° until equilibrium was attained, three days being found to be a sufficient time. The saturated solution was analyzed for carbonate by titration against acid, using methyl orange as indicator, with correction for the effect of the sulfate on the end-point. Water was determined as loss by evaporation from platinum dishes. Sulfate was determined only when the amounts had become small, in Line 6 by precipitation as barium sulfate from an acid solution, and in Lines 7, 8 and 9 turbidimetrically. Direct weighing of small pipetted samples gave values for the density of the solution.

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[1] Blasdale, THIS JOURNAL, **45**, 2935 (1923).

[2] Teeple, "Industrial Development of Searles Lake Brines," Chemical Catalog Company, New York, **1929**, p. 72.

TABLE I

SYSTEM K_2SO_4–K_2CO_3–H_2O AT 25°

No.	Original complex K_2SO_4, wt. %	Original complex K_2CO_3, wt. %	Saturated solution K_2SO_4, wt. %	Saturated solution K_2CO_3, wt. %	Density	Solid phase
1	..	..	10.7	..	1.083	K_2SO_4
2	21.8	4.6	6.5	5.5	1.103	K_2SO_4
3	17.2	8.3	4.9	9.4	1.122	K_2SO_4
4	17.1	14.1	2.8	16.4	1.170	K_2SO_4
5	13.7	20.4	1.5	23.2	1.230	K_2SO_4
6	14.6	30.1	0.3	35.0	1.348	K_2SO_4
7	8.1	41.5	.08	45.1	1.465	K_2SO_4
8	16.6	40.6	.03	48.6	1.506	K_2SO_4
9	8.4	51.6	.03	52.8	1.557	K_2SO_4 +
	2.1	54.8				$K_2CO_3\cdot 3/2H_2O$
10	..	..	..	52.8	1.557	$K_2CO_3\cdot 3/2H_2O$

It appears from the table, and also from the figure, that the solubility of the potassium sulfate is reduced to less than 0.1% when the solution is still far from saturation with respect to carbonate, and to 0.03% at the saturation point. It is striking that the solubility is so greatly lessened by the presence of potassium carbonate; so great a salting-out effect upon a reasonably soluble salt is not common.

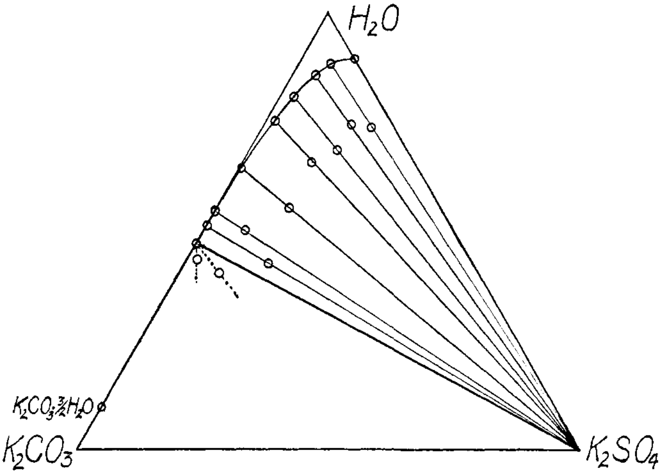

Fig. 1.—25° Isotherms for K_2CO_3–K_2SO_4–H_2O.

Especial attention was paid to the question of possible solid solution of the two salts, since the corresponding sodium salts form the well-known solid solution Glaserite. Algebraic extrapolations of the tie lines from saturated solution through original complex all fell somewhat short of the point representing 100% K_2SO_4, by a matter of several tenths of 1% up to over 1%. Two crystallization experiments, however, from solution rich in carbonate gave solids which analyzed at 99.89 and 99.91% of K_2SO_4, respectively, after correction for the small amount of adhering solution; from this we conclude that the direction of the tie lines was influenced by a small systematic error in the analytical work and that solid solution does not occur in the system at 25° to a measurable extent.

Summary

The solubility of potassium carbonate and potassium sulfate in the ternary system with water at 25° has been measured. Solid solution has not been found to occur.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A GENERAL METHOD OF MEASURING THE PARTIAL PRESSURE OF MERCURY AT ROOM TEMPERATURES

BY L. L. HIRST AND A. R. OLSON

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Two methods of determining the activities of amalgam constituents have been used. In the first of these methods the calculation is based on measurements of the electromotive forces of concentration cells. This method has been used successfully in investigating a number of amalgams. In some cases, however, a serious difficulty is encountered. Thus with cesium and barium amalgams, no liquid is known which dissolves enough of the salt to make the liquid sufficiently conducting, and which at the same time is unreactive enough so that no side reactions occur with the metal. In the second method, vapor pressures of amalgams have been measured at high temperatures. The data so obtained must be extrapolated to 25° in order to be used in connection with other data. Because of these difficulties, we have devised a general method of obtaining the partial pressures of mercury over any amalgam at room temperatures.

When light from a mercury arc under properly controlled conditions falls on mercury vapor, the resonance line 2536 Å. is absorbed according to the equation $I = I_0e^{-\alpha pd}$, in which I is the intensity of the transmitted light, I_0 is the intensity of the incident light and α, p and d are the absorption coefficient, the pressure of mercury and the thickness of the absorbing gas layer. If α were a constant, we could determine p directly by measuring the quantity I/I_0. However, it has been shown by Hughes and Thomas[1] that α is not a constant even when a mercury resonance lamp is substituted for the mercury arc. α is also affected by the pressure of foreign gas even though these gases themselves have a negligible absorption for this line. Fortunately it was possible to determine p without evaluating α.

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[1] Hughes and Thomas, *Phys. Rev.*, **30**, 466 (1927).