which the empirical equation $X = Y^m$ was advanced, these measurements, together with similar studies from this Laboratory, will be considered, in a subsequent publication, for the purpose of deriving some generalization relating the distribution ratio of these isomorphous salts between liquid and solid phases, to the molar solubilities of the individual salts in the pure solvent.

Summary

1. The following ternary systems have been studied at 25°

$Mg(NH_4)_2(SO_4)_2–Cu(NH_4)_2(SO_4)_2–H_2O$
$CuK_2(SO_4)_2–NiK_2(SO_4)_2–H_2O$
$CoK_2(SO_4)_2–CuK_2(SO_4)_2–H_2O$
$ZnK_2(SO_4)_2–CuK_2(SO_4)_2–H_2O$
$ZnK_2(SO_4)_2–NiK_2(SO_4)_2–H_2O$
$Cu(NH_4)_2(SO_4)_2–CuK_2(SO_4)_2–H_2O$

2. Continuous series of solid solutions were found in each case.

3. The results, considered from the point of view of Roozeboom's classifications of solid solutions, show all these systems to belong apparently to Type I of that classification.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

Freezing Point and Solubility Data for the System Chlorine Monoxide–Water

BY C. H. SECOY AND G. H. CADY

It is known that chlorine monoxide dissolves in water to give hypochlorous acid but no previous study has been made of the possible existence of hydrates of this acid nor have highly concentrated solutions of the acid been prepared and studied. In this work freezing point and solubility data have been obtained for the system chlorine monoxide–water. The only pertinent data found in the literature were the freezing point of pure chlorine monoxide, reported by Goodeve[1] to be −116°, and the freezing points of very dilute solutions of hypochlorous acid.[2]

Experimental

Preparation of Chlorine Monoxide and Hypochlorous Acid.—Chlorine monoxide was prepared by passing a stream of dry chlorine mixed with air up through a column of yellow mercuric oxide.[3] A 35-mm. glass tube, one meter long, was filled with mercuric oxide with a sufficient quantity of porcelain chips added to prevent packing. The top of this tube was sealed to 8-mm. glass tubing leading to a 24 mm. × 30 cm. test-tube fitted with a stirrer and a thermocouple well. Other workers[3] have stated that the mercuric oxide previously should be heated to 400°, for a period of an hour or longer. This treatment, however, was not used since it has been found that it is neither necessary nor helpful.[4] The spent mercuric oxide was recovered by precipitation in the cold with sodium hydroxide, washed free of sodium hydroxide, and dried at 120°.[4] The air and chlorine were dried by bubbling through sulfuric acid and passed through a T-tube into the mercuric oxide. The rate of flow of the air was about twice that of the chlorine. The air prevented any noticeable heating effect from the reaction.

The chlorine monoxide was condensed by means of a dry-ice–alcohol cooling mixture, and hypochlorous acid of the desired concentration was then obtained by adding the required amount of water and stirring until equilibrium had been reached. Chlorine monoxide and strong hypochlorous acid were found to be stable over a period of a week if kept at a temperature below −20°. However, some free chlorine invariably was formed if the solution was allowed to stand for a few hours at a higher temperature.

Temperature Measurements.—Freezing point data were obtained by thermal analysis. Temperatures were measured by a copper–constantan thermocouple calibrated at the ice-point, the dry-ice point, and the boiling point of oxygen. The conversion table reported by Giauque, Buffington, and Schulze[5] was used after applying a constant factor, characteristic of the thermocouple used, to the e. m. f. readings. The use of this factor allowed points at the calibration temperatures to fall within 0.02° of Giauque's curve. The e. m. f. was measured with a Leeds and Northrup Type K potentiometer using a voltage-sensitive galvanometer. Readings were made to the nearest tenth of a microvolt and temperatures obtained were believed to be accurate to 0.1°. The warm junction of the thermocouple was kept at the temperature of melting ice.

Method of Analysis.—The method reported by Spinks[6] was used to determine both free chlorine and available chlorine in the form of chlorine monoxide and/or hypochlorous acid. The sample, from 0.2 to 0.5 g., was transferred by means of a pipet to a weighed flask containing a

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[1] Goodeve, *J. Chem. Soc.*, 2733 (1930).

[2] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

[3] "Gmelins Handbuch der anorganischen Chemie," 8th Ed., Vol. 6, "Chlor," Verlag Chemie, Berlin (1927), p. 228; Balard, *Ann. chim. phys.*, [2] **57**, 225 (1834); *Taylors Scientific Memoirs*, **1**, 269 (1837); Pelouze, *Ann. chim. phys.*, [3] **7**, 176 (1843).

[4] Muskat and Cady, U. S. Patent 2,155,281 (1939).

[5] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[6] Spinks, *ibid.*, **53**, 3015 (1931).

solution of potassium iodide. The flask was then reweighed to determine the weight of the sample. The determination of the free chlorine served as a check on the possible decomposition of the hypochlorous acid, and no data were used from any sample which showed chlorine to be present.

The composition of the dihydrate, $HOCl \cdot 2H_2O$, was established by direct analysis of the crystals formed by partially freezing solutions of concentrations just above and just below 16.6 mole % chlorine monoxide. Both phases were analyzed after being separated quickly by filtration in a small centrifuge. The filter consisted of a piece of glass cloth fused to the end of a tube drawn and cut to just fit in a small test-tube which could be used in the centrifuge. After previously cooling the filter tube with dry-ice, the partly frozen slush was added to it and centrifuged for ten or fifteen seconds. The dry crystals were then transferred to a flask containing a solution of potassium iodide, weighed, and titrated. The data obtained are summarized in Tables I and II.

TABLE I

FREEZING POINTS OF WATER SOLUTIONS OF Cl_2O

Mole % Cl_2O	F., °K.	Solid phase
2.7	267.2	Ice
3.9	264.4	Ice
5.9	259.4	Ice
7.9	253.5	Ice
8.4	251.0	Ice
10.0	245.1	Ice
10.6	242.5	Ice
11.7	233.5	Eutectic
11.9	234.2	$HOCl \cdot 2H_2O$
12.0	234.5	$HOCl \cdot 2H_2O$
12.5	235.3	$HOCl \cdot 2H_2O$
13.1	235.8	$HOCl \cdot 2H_2O$
13.7	236.3	$HOCl \cdot 2H_2O$
14.4	236.6	$HOCl \cdot 2H_2O$
15.1	236.8	$HOCl \cdot 2H_2O$
15.4	236.9	$HOCl \cdot 2H_2O$
16.1	237.0	$HOCl \cdot 2H_2O$
16.6	237.1	$HOCl \cdot 2H_2O$
17.5	237.1	$HOCl \cdot 2H_2O$
18.7	237.0	$HOCl \cdot 2H_2O$
19.5	236.9	$HOCl \cdot 2H_2O$
20.7	236.8	$HOCl \cdot 2H_2O$

TABLE II

IDENTIFICATION OF THE SOLID COMPOUND

Mole % Cl_2O	
Liquid	Solid
14.6	16.3
16.4	16.8
16.9	16.7
17.3	16.3
18.0	16.5

Solubility of Chlorine Monoxide in Water.—The two liquid phases were held at the temperature desired and stirred until equilibrium was established. After allowing any suspended oily drops of chlorine monoxide to settle from the water layer, a sample of the latter was taken for analysis. Measurements were not attempted at temperatures above 264°K., because of the high vapor pressure and the tendency for decomposition to occur at higher temperatures. Results are tabulated in Table III.

TABLE III

SOLUBILITY OF Cl_2O IN H_2O

Temp., °K.	Mole % Cl_2O	Temp., °K.	Mole % Cl_2O
263.8	22.9	244.2	20.3
259.9	22.1	241.2	20.4
257.3	21.7	240.0	20.5
251.1	20.6	238.4	20.6
247.4	20.1	236.8	20.7
246.4	20.0		

Solubility of Water in Chlorine Monoxide.—A 100-cc. flask containing phosphorus pentoxide was fitted with a glass cap, designated cap A, which slid down over the neck of the flask. The cap was made tight by fitting a short piece of rubber tubing over the neck of the flask and the cap. A second similar cap, designated cap B, was connected by a side arm to a potassium iodide absorption train. A glass tube extended through the top of cap B to the surface of the phosphorus pentoxide when the flask was in place. Saturation of the chlorine monoxide was obtained by adding sufficient water to form the double layer and stirring at constant temperature until equilibrium was reached. The samples were taken by means of a dipper constructed by blowing a small bulb in the end of a piece of 6 mm. glass tubing. A side opening was then blown just above the bulb and about 2 cm. from the end of the tube. In order to remove a sample not contaminated with the water layer, a piece of 10 mm. tubing was inserted into the solution, the water layer forced outside of this tube with compressed air, and the dipper used inside the tube.

After being weighed, with cap A in place, the flask was cooled with dry-ice and a sample of the chlorine monoxide saturated with water at the desired temperature was added. The flask was then attached to the absorption train by means of cap B, and, as the temperature rose, a slow current of air dried by phosphorus pentoxide was drawn through the system until all of the chlorine monoxide had evaporated. Cap A was then replaced and the flask weighed, the increase in weight giving the weight of water in the sample. The amount of chlorine monoxide in the sample was determined by titrating the liberated iodine. Results are given in Table IV.

TABLE IV

SOLUBILITY OF H_2O IN Cl_2O

Temp., °K.	Mole % H_2O
270.0	3.4
236.8	2.9
194.6	1.8

The Freezing Point of Pure Chlorine Monoxide.—Cooling curves taken with a freshly prepared sample of chlorine monoxide, dried by passing the gas over phosphorus pentoxide, gave a freezing point of −120.6°. After adding water to the chlorine monoxide and stirring to secure saturation, the freezing point was found to be

−121.0°. Phosphorus pentoxide was then added directly to the liquid and again a freezing point of −120.6° was observed.

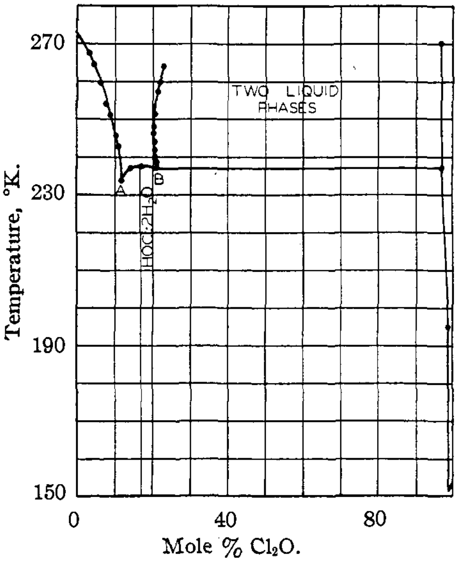

Fig. 1.—Temperature–concentration diagram for the system chlorine monoxide–water. Several experimentally determined points between A and B have been omitted on the graph (see Table I for data).

Due to the discrepancy between this result and the value of −116°, reported by Goodeve,[1] the thermocouple was recalibrated at the boiling point of oxygen. A fresh sample of chlorine monoxide, dried as before, was prepared. In order to free the chlorine monoxide from dissolved air and chlorine, approximately one-fourth of the sample was distilled off at about −75°. The freezing point then observed was −120.6°. After removing a second portion of the chlorine monoxide in the same manner, the same freezing point was obtained. Addition of water gave the same depression of 0.4°, as previously found.

The temperature–concentration diagram for the system is shown in Fig. 1. Point B, at 20.7 mole % chlorine monoxide and 236.8°K., is an invariant point representing equilibrium between two liquid phases, the solid phase and the gaseous phase. It is to be noted that solid HOCl is not obtained. A solution containing a sufficiently high concentration of chlorine monoxide to give the compound HOCl would separate into two liquid phases before freezing and give, as the solid phase, the hydrate, $HOCl \cdot 2H_2O$.

Summary

The freezing point–composition diagram for the system chlorine monoxide–water has been studied over the entire range, and solubilities of chlorine monoxide in water and of water in chlorine monoxide have been measured. Chlorine monoxide and water are a pair of partially miscible liquids. The solid phase formed from solutions of concentration greater than 11.7 mole % chlorine monoxide has the composition $HOCl \cdot 2H_2O$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXX. The Fluorescence of Biacetyl. Some General Considerations Governing the Study of Fluorescence

BY F. C. HENRIQUES, JR., AND W. ALBERT NOYES, JR.

Recent studies of the fluorescence of acetone have shown that under some conditions a Stern-Volmer equation is at least approximately obeyed[1] but that if the intensity of the incident radiation is sufficiently high, noticeable increase of fluorescence with time is observed.[2] Moreover, the three intense bands of acetone fluorescence were shown to be identical with those of biacetyl. It also has been shown that the main portions of the fluorescences of acetaldehyde and of methyl ethyl ketone are identical with those of biacetyl and of acetone.[3] It seems probable, therefore, that the fluorescing molecule is the same in all of these cases and that it is probably biacetyl.

Several questions still remain unanswered concerning the so-called fluorescence of acetone, particularly those having to do with the mechanism whereby the biacetyl molecule is excited when acetone is the absorber. It has seemed advisable, therefore, to investigate the effect of certain variables on the fluorescence of biacetyl. The fluorescence of this molecule has been investigated

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[1] Fisk and Noyes, *J. Chem. Phys.*, **2**, 654 (1934).

[2] Matheson and Noyes, THIS JOURNAL, **60**, 1857 (1938).

[3] Matheson and Zabor, *J. Chem. Phys.*, **7**, 536 (1939).