# 210. *The System Cupric Selenate–Water–Selenic Acid at 25°.*

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THE system cupric sulphate–water–sulphuric acid has been investigated by several workers (Bell and Tabor, *J. Physical Chem.*, 1908, **12**, 171; Foote, *J. Amer. Chem. Soc.*, 1915, **37**, 288; Cameron and Crockford, *J. Physical Chem.*, 1929, **33**, 709; Posnjak and Tunell, *Amer. J. Sci.*, 1929, **18**, 1; Crockford and Warwick, *J. Physical Chem.*, 1930, **34**, 1065), but the related selenium system does not appear to have been systematically examined. The present paper describes such an investigation of the 25° isotherm. By determining the aqueous vapour pressure of selenic acid solutions, that of the pentahydrate of cupric selenate has been deduced.

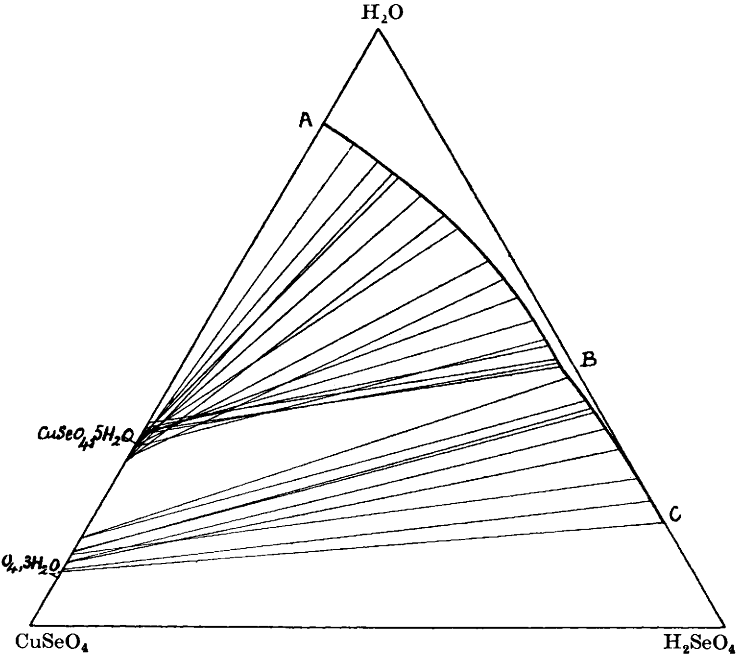
## EXPERIMENTAL.

*Preparation of Materials.*—A modification of Dennis and Koller's method (*J. Amer. Chem. Soc.*, 1919, **41**, 956) was used in the preparation of copper selenate and selenic acid. Powdered selenium (50 g.) was oxidised to dioxide by fairly concentrated nitric acid, the excess of which was then removed by repeated evaporation to dryness. A filtered solution of the dioxide in 5 l. of water was treated with a slow current of chlorine whilst, at the same time, basic copper carbonate (350 g.) was added gradually with constant stirring to prevent the separation of a basic salt which does not redissolve; cessation of effervescence on further addition marked the end of the reaction. The resulting solution, containing copper selenate, chloride, and some carbonate, after being filtered, evaporated to smaller bulk, and cooled, gave crystals of $CuSeO_4,5H_2O$. These were collected, washed quickly with water, and recrystallised. At 105° the pentahydrate is converted into the monohydrate and this was used in preparing the majority of the mixtures used.

The whole of the copper in a concentrated solution of selenate was precipitated by hydrogen sulphide, the sulphide rapidly filtered off and the solution concentrated at 100° under 10 mm. pressure until it contained approximately 82% of selenic acid; this was free from selenious acid and from copper.

*The System* $CuSeO_4$–$H_2O$–$H_2SeO_4$.—Thick-walled test-tubes containing $CuSeO_4,H_2O$ with aqueous selenic acid of various strengths were securely stoppered and shaken in a thermostat at 25° ± 0·05° for periods varying from 10 days with the more dilute acid to 4 weeks with the more concentrated acid. The separation of solid and liquid phases was then effected by rapid filtration, a few seconds sufficing with the more aqueous solutions but a greater time (about 10 mins.) being required with the more viscous concentrated acid solutions. No temperature control was maintained during filtration partly because the laboratory temperature was above 15° and partly because (i) for less acid solutions filtration was so rapid and (ii) for concentrated acid solutions the solubility of the copper selenate was always below 2% (see curve BC, Fig. 1). Furthermore, a change in the composition of the solid phase was improbable, since this could be brought about only by transition to another hydrate.

FIG. 1.



The solids were analysed in a moist state. For analysis a weighed sample of liquid or solid was either diluted with or dissolved in water and the percentage of free selenic acid was estimated by titration with *N*-sodium hydroxide. The blue colour of the copper ion was found to enhance rather than to decrease the precision with which the end-point could be observed with methyl-orange as indicator, and hydrolysis of the selenate did not interfere. The copper present in the liquid after titration was estimated by precipitation from the boiling solution with sodium hydroxide, filtering, washing, and redissolving the precipitate, and titrating the solution iodometrically. Removal of selenate ion before titration of the copper was necessary by reason of its slow reaction with potassium iodide. This method of estimation was preferable to an electrolytic one (against which, however, it was repeatedly checked) in consequence of cathodic reduction of selenates to free selenium and the resulting contamination of the copper deposits.

Table I gives the results from 32 experiments. These are plotted upon the triangular diagram (Fig. 1), points relating to the moist salt and the corresponding liquid phase being joined and the line continued to the $CuSeO_4$–$H_2O$ axis.

TABLE I.

| Solid phase (moist). | | Liquid phase. | | Solid phase (moist). | | Liquid phase. | |
|---|---|---|---|---|---|---|---|
| $CuSeO_4$, %. | $H_2SeO_4$, %. | $CuSeO_4$, %. | $H_2SeO_4$, %. | $CuSeO_4$, %. | $H_2SeO_4$, %. | $CuSeO_4$, %. | $H_2SeO_4$, %. |
| 64·71 | 0·09 | 15·89 | 0·00 | 53·27 | 12·43 | 1·98 | 50·16 |
| 62·60 | 1·27 | 13·44 | 6·16 | 49·38 | 14·10 | 1·92 | 51·10 |
| 63·68 | 1·48 | 11·77 | 11·07 | 43·95 | 18·60 | 1·91 | 53·46 |
| 61·72 | 1·71 | 11·84 | 11·11 | 49·03 | 15·95 | 2·24 | 53·83 |
| 59·96 | 3·22 | 10·48 | 14·23 | 43·79 | 20·24 | 2·01 | 54·03 |
| 63·43 | 2·59 | 10·59 | 14·57 | 49·92 | 14·94 | 1·97 | 54·39 |
| 62·00 | 1·88 | 10·09 | 15·27 | 52·66 | 22·68 | 1·96 | 56·66 |
| 62·67 | 2·61 | 7·96 | 20·25 | 42·55 | 31·03 | 0·97 | 61·05 |
| 57·36 | 5·92 | 6·79 | 25·06 | — | — | 1·08 | 61·30 |
| 63·63 | 2·25 | 5·49 | 28·28 | 57·95 | 21·78 | 0·89 | 62·82 |
| 58·29 | 6·33 | 3·85 | 35·32 | 48·76 | 28·33 | 1·12 | 63·08 |
| 63·40 | 3·13 | 3·94 | 35·39 | 51·44 | 28·03 | 0·70 | 66·00 |
| 55·69 | 9·32 | 3·15 | 38·96 | 52·72 | 28·91 | trace | 70·36 |
| 55·27 | 8·68 | 2·64 | 42·39 | 46·77 | 35·58 | 0·00 | 75·01 |
| 55·98 | 8·54 | 2·82 | 42·55 | 47·19 | 37·93 | 0·00 | 78·43 |
| 42·60 | 18·04 | 2·19 | 46·77 | 46·10 | 40·73 | 0·00 | 82·42 |

Dennis and Koller (*loc. cit.*) record that a hydrate, $CuSeO_4,3H_2O$, remained after $CuSeO_4,5H_2O$ had been refluxed with acetone for 10 hours. This was confirmed (Found : $CuSeO_4$, 79·25. Calc. for $CuSeO_4,3H_2O$ : $CuSeO_4$, 79·30%), but repeated refluxing with fresh portions of acetone led to further dehydration (Found : $CuSeO_4$, 85·57%).

*The Aqueous Vapour Pressure of* $H_2SeO_4$–$H_2O$ *Mixtures.*—Mixtures of selenic acid, prepared by Messrs. British Drug Houses, with appropriate quantities of recently-boiled distilled water were introduced into bulb *A* which was then attached by a perfectly fitting ground joint to the apparatus shown in Fig. 2 (an improvement due to Dr. P. L. Robinson, and not hitherto described, of an apparatus originally devised by Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412). The apparatus was then evacuated at *D*, with taps *E* open and *F* shut, by means of a " Hyvac " pump working through an efficient drying train. The temperature was so adjusted that the liquid in *A* evaporated rapidly without ebullition, and it was found that the stream of vapour so produced was an effective means of removing residual gas from the apparatus. Following this degassing, which lasted for ½ hour, the level of the mercury was raised from bulb *C* to U-tube *B* by closing tap *E* and admitting air at tap *F*. The apparatus was then placed in a thermostat at 25° ± 0·05°, and after a suitable time had been allowed for attainment of equilibrium, the difference in mercury levels in the U-tube was measured by means of a cathetometer reading to 0·2 mm. Experience showed that a sufficient flushing out with vapour resulted in a static pressure being recorded very quickly, but failing this rigorous removal of gas, a creep of pressure was observed which continued over many hours. With thoroughly out-gassed liquid, the pressures recorded are believed to be within ± 0·1 mm. of the true vapour pressure. The composition of each mixture studied was ascertained with an accuracy of one part in 500 parts by filling the apparatus with air, removing the bulb *A*, and titrating a sample of its contents with *N*-sodium hydroxide. The results (Table II), corrected for mercury at 0°, when plotted (Fig. 3, upper curve) are similar in form to Sorel's (*Z. angew. Chem.*, 1899, 272; Fig. 3, lower curve) for aqueous sulphuric acid.

Fig. 2.

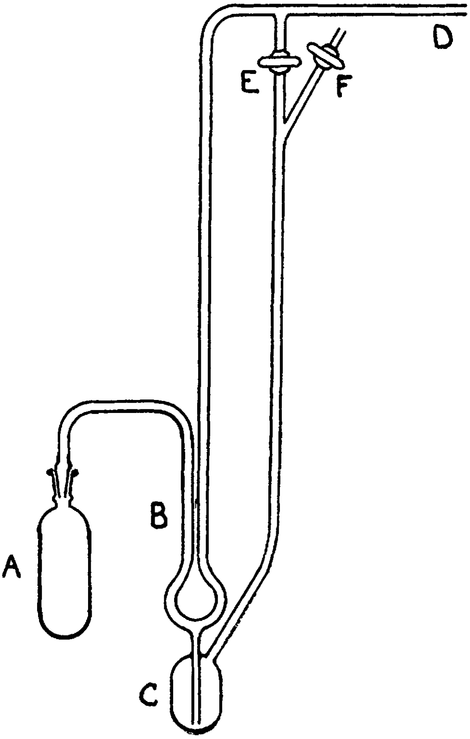
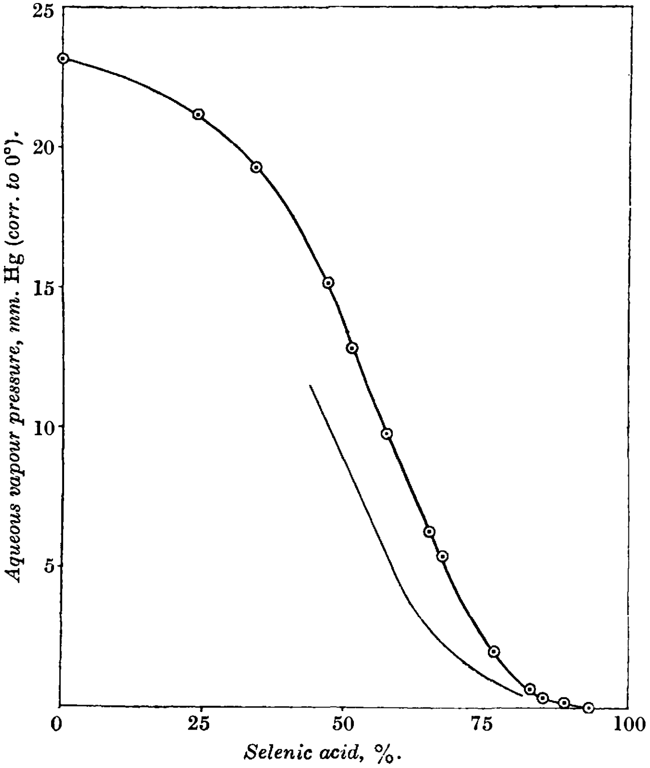


TABLE II.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2SeO_4$, % .................... | 0·00 | 23·93 | 34·13 | 47·08 | 51·34 | 57·58 | 65·30 |
| Vap. press. (corr.) (mm. Hg) | 23·21 | 21·21 | 19·25 | 15·11 | 12·79 | 9·75 | 6·22 |
| $H_2SeO_4$, % .................... | 67·58 | 76·69 | 83·18 | 85·48 | 89·29 | 93·50 | |
| Vap. press. (corr.) (mm. Hg) | 5·38 | 1·96 | 0·62 | 0·32 | 0·18 | 0·03 | |

FIG. 3.



## *Discussion of Results.*

It is evident from Fig. 1 that the co-ordination lines of the region *A* to *B* come to a focus at the composition represented by the pentahydrate. The unbroken curve *BC* is indicative of the presence of one lower hydrate only. The hygroscopic nature of the materials rendered the analytical data for the moist solids of this region less precise, with the result that the co-ordination lines afford a less certain indication of the composition of the pure solid phase; they do suggest, however, that only the monohydrate exists. Furthermore, high viscosity in this region led to the retention of a considerable amount of mother-liquor and, the points being thereby removed so far from the focus, a slight absorption of water tended appreciably to alter the direction of the co-ordination lines. A useful confirmation of the view that only the pentahydrate and monohydrate exist under the prescribed conditions was given by a microscopical examination of the solid phases, which disclosed only two materials: well-formed blue crystals between *A* and *B*, and minute, almost white, crystals between *B* and *C*.

Fig. 1 shows that 55% selenic acid is the highest concentration in which $CuSeO_4,5H_2O$ can continue to exist at 25°. Fig. 3 shows that the aqueous vapour pressure of this acid is 11·0 mm. Neglecting the effect of approx. 2% of dissolved copper selenate upon the vapour pressure of selenic acid, we may therefore infer that the vapour pressure of $CuSeO_4,5H_2O$ at 25° is approx. 11·0 mm.

The vapour pressure of $CuSeO_4,H_2O$ could not be similarly determined because in no case was the phase anhydrous $CuSeO_4$ obtained.

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