

Technical Papers

The Saturation Curves of Cinnabar and Metacinnabar in the System $\text{HgS}-\text{Na}_2\text{S}-\text{H}_2\text{O}$ at 25°C^1

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In connection with an investigation of quicksilver ore deposits, the objective of which is to learn more about the physico-chemical processes by which they originated, we have determined at 25°C the portions of the saturation curves of cinnabar and metacinnabar in the system $\text{HgS}-\text{Na}_2\text{S}-\text{H}_2\text{O}$ that extend from the H_2O corner of the triangle to points beyond the line H_2O -equals-75-percent-by-weight. We are continuing this work and shall carry it to higher temperatures approaching 100°C as nearly as is possible with an open thermostat.

Preparing and purifying reagents and solutions. The Baker and Adamson reagent grade red HgS (artificial cinnabar) used in this experiment contained substances insoluble in Na_2S . Leaching with sodium hydroxide reduced the content of such impurities to less than 0.01 percent. Black HgS (artificial metacinnabar) was made by dissolving red HgS in Na_2S solution and precipitating as black HgS . 'Baker Analyzed' Reagent grade $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was rinsed with distilled water, and clear colorless material was set aside for use. Saturated Na_2S stock solution was made up from boiled distilled water in an oxygen-free nitrogen atmosphere.

Establishing equilibrium. Bottles containing fine-grained red or black HgS and solutions of Na_2S were rotated in a constant temperature bath at 25.00°C ($\pm 0.03^\circ \text{C}$) for periods of time ranging from 10 hr to several weeks. Na_2S and HgS content of solutions from cinnabar-solution mixtures (two-phase) kept in the bath for 1 wk agreed with the Na_2S and HgS content of solutions from cinnabar-solution mixtures kept in the bath for 2 wk and longer, indicating that equilibrium was closely approximated. Metacinnabar-solution mixtures (two-phase) were kept in the bath 24 hr or less because of the tendency of metacinnabar to invert slowly to cinnabar. Samples containing less than 3 percent by weight of Na_2S were kept in the bath for 24 hr, and those containing more than 6 percent by weight Na_2S for 10 hr. Solution compositions plotted on the triangular diagram fall on a smooth curve, indicating that metastable equilibrium between metacinnabar and Na_2S solutions was attained. The identity of the solid phases was established by means of the x-ray spectrometer and by means of the optical microscope. The optical method was found to be much more

TABLE 1. Solubility of cinnabar in sodium sulfide solutions at 25.00°C ($\pm 0.03^\circ \text{C}$).

Percentage by weight		
Na_2S	HgS	H_2O (by difference)
0.95	0.21	98.84
1.50	.57	97.93
2.31	1.34	96.35
3.58	2.91	93.51
4.37	4.12	91.51
6.07	7.29	86.64
9.64	15.59	74.77

TABLE 2. Solubility of metacinnabar in sodium sulfide solutions at 25.00°C ($\pm 0.03^\circ \text{C}$).

Percentage by weight		
Na_2S	HgS	H_2O (by difference)
0.51	0.11	99.38
1.37	.79	97.84
2.85	2.76	94.39
6.55	10.24	83.21
10.93	20.70	68.37

sensitive than the x-ray method for detecting slight traces of cinnabar in the metacinnabar; no cinnabar was found in samples that contained less than 3 percent Na_2S , and only a trace (less than 0.1 percent) of cinnabar was detected in samples that contained more than 6 percent Na_2S .

Method of analysis. The saturated solutions were analyzed for mercury, sodium, and sulfur. In preparation for analysis, the solutions were quickly filtered through a fritted glass crucible to remove suspended solid HgS . To a sample of saturated solution, previously weighed into a beaker and diluted with water, concentrated hydrogen peroxide solution (30 percent H_2O_2) was added. The excess sulfide oxidized to sulfate, diminishing the sulfide-ion concentration and causing mercury to precipitate as black mercuric sulfide. The black HgS was filtered in a fritted glass crucible, weighed, and the concentration of HgS was calculated in grams HgS per gram solution. The filtrate was analyzed for sodium or sulfate by weighing as sodium sulfate or barium sulfate, respectively, and the Na_2S concentration was calculated. Water content was determined by difference. The analytical data are presented in Tables 1 and 2.

The saturation curves of cinnabar and metacinnabar at 25°C . The portions of the saturation curves of cinnabar and metacinnabar in the system $\text{HgS}-\text{Na}_2\text{S}-\text{H}_2\text{O}$ at 25°C from the H_2O corner to points beyond the line H_2O -equals-75-percent-by-

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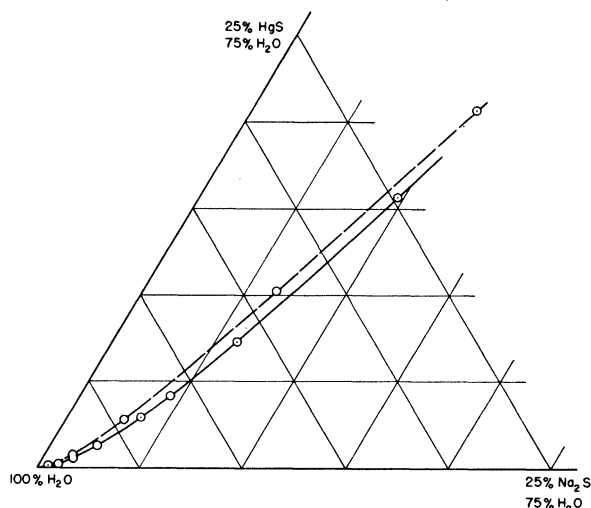


FIG. 1. The saturation curves of cinnabar and metacinnabar in the system $\text{HgS}-\text{Na}_2\text{S}-\text{H}_2\text{O}$ at 25°C from the H_2O corner to points beyond the line H_2O -equals-75-percent-by-weight. The dashed line represents the saturation curve of metacinnabar; the solid line, the saturation curve of cinnabar. The small circles represent analyses of saturated solutions.

weight are shown in Fig. 1. The analyses of the solutions saturated with cinnabar and with metacinnabar at 25°C are represented by small circles in this figure.

Previous work by Knox (1) had shown that in Na_2S solutions there is a marked increase of solubility of cinnabar and metacinnabar with increasing concentration of Na_2S . Knox determined the concentrations of HgS in the saturated solutions in grams per cubic centimeter, and his data were therefore insufficient to determine the exact positions of the saturation curves in a triangular equilibrium diagram.

Reference

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Effect of Cortisone on Experimental Murine Typhus in Mice¹

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Studies concerning the effect of cortisone and other adrenal cortical hormones on infectious diseases have attracted considerable attention during the past few years. Cortical hormones have been shown to increase the susceptibility in a number of hosts to many unrelated bacterial and viral diseases (1). Owing to the lack of a highly susceptible animal for studying experi-

mental infections with typhus rickettsiae, the possibility that cortisone might enhance the susceptibility of mice to murine typhus seemed worthy of investigation.

The inoculum used in these experiments consisted of yolk-sac material infected with *Rickettsia mooseri*. Heavily infected yolk sacs harvested from viable chick embryos were diluted to 10 percent by weight with 0.5 percent sterile skim milk and ground in a sterile cold Waring Blender for 10 sec. Immediately prior to inoculations for infectivity titrations, the inoculum was titrated by the mouse toxicity test (2) to provide information on the relative potency of the inoculum used for each experiment. Twofold dilutions (1:10 to 1:10,240) were inoculated intraperitoneally in 0.5-ml amounts in the infectivity tests.

Four strains of mice were tested: albino, C strain, NHF_8 (3), and dba mice, which ranged in weight from 15 to 22 g (4). The cortisone was injected subcutaneously in 0.2-ml doses (5).

TABLE 1. Effect of cortisone on the susceptibility of various strains of mice to murine typhus.

Cortisone dosage (mg)	Strain of mice infectious LD_{50}					
	White*	C*	White*	NHF_8 *	White†	Dba†
1.25	1280	2580	1280	4190	1600	1280
2.5					3900	2560
5.0					< 5120	10240
0.0	185	690	185	115	240	200

* Toxic dose 1:50.

† Toxis dose 1:65.

To determine the effects of varying dosage of cortisone on their susceptibility, white mice were given 0.625, 1.25, 2.5, 5.0, and 10.0 mg cortisone 4 hr prior to injection of the infectious suspension. No adverse effects of cortisone treatment were evident in control mice when 5.0 mg or less was used, whereas 10.0 mg produced several deaths on the 7th and 8th days after inoculation. Mice were observed for a period of 10 days. By using an inoculum with a toxic LD_{50} of 1:130, the following infectious LD_{50} s (6) were obtained: mice receiving no cortisone, 1:250; 0.625 mg, 1:1280; 1.25 mg, < 1:2560; 2.5 mg, 1:1750; and 5.0 mg, 1:1500. The results of this experiment indicated that the use of as little as one pretreatment of 0.625 mg greatly increased the susceptibility of white mice to murine typhus infections.

To determine the best time to administer the cortisone relative to the injection of infectious material, white mice were given a single dose of 1.25 mg of cortisone at 0, 4, 7, 16, 20, and 24 hr prior to infection and 24 hr after infection. The maximum effectiveness of 1.25 mg of cortisone was reached 4 to 16 hr after it was administered subcutaneously. The period of maximum effectiveness of other dosages of cortisone given subcutaneously to mice was not determined. Using an inoculum with a toxic LD_{50} of 1:14, the

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