

6. For sucrose solutions the surface tension equation reduces to

$$\sigma - \sigma_0 = RTkc$$

which is in agreement with the data of Jones and Ray.

7. For the lower molecular weight fatty acids, the surface tension equation reduces to

$$\frac{\sigma}{\sigma_0} = 1 - B \log \left[1 + \frac{c}{A} \right]$$

which is the well-known empirical equation of Szyszkowski. The interpretation of the constants of the Szyszkowski equation resulting from the theory of this paper is closely similar to the conclusions of Langmuir published many years ago.

8. In very dilute solutions the surface tension

decreases linearly with the concentration. Over this range the adsorption potential can be calculated from the equation

$$-W = RT \ln \left[1 + \frac{1}{RTk} \left\{ \frac{d(\sigma_0 - \sigma)}{dc} \right\}_0 \right]$$

an equation resulting from the theory of this paper and being identical with a similar equation of Langmuir derived in a different way.

9. The adsorption potential for negative ions is negative, is about ten times greater in absolute magnitude than the positive adsorption potential calculated from the mirror-image equation and is of the same order of magnitude as the adsorption potentials found by Langmuir for fatty acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Ternary System Selenium Dioxide-Barium Selenite-Water at 0, 25, and 50°

BY JOSEPH L. NEAL, JR., AND C. R. McCROSKY

Although they have been known for over one hundred years, the salts of selenious acid have received comparatively little attention. Analyses and qualitative descriptive studies were made by Berzelius,¹ Muspratt,² Nilson,³ and Boutzourcano.⁴ Recently the solubilities in water and the transition points of the selenites of sodium, potassium,⁵ and ammonium⁶ have been studied. Quantitative solubility measurements upon the other selenites are entirely lacking. Such data are of interest in connection with certain efforts which are being made in this Laboratory to utilize these salts in analytical and preparative processes. As a step toward these ends, this report deals with the results of a study of the ternary system selenium dioxide-barium selenite-water at three temperatures. We hope later to present data for the corresponding systems of the other alkaline earth selenites.

Experimental

Materials.—Selenium dioxide was prepared by the oxidation of crude black selenium (supplied through the

courtesy of the United States Metals Refining Co.) with nitric acid, and purified by repeated sublimation.

Selenious acid was prepared by dissolving the purified dioxide in a small excess of hot water, cooling and inoculating, if necessary. The crystals were dried on a porous plate, without the use of a desiccant. An analysis of a typical lot showed SeO₂, 85.79%; calcd. 86.06%. The crystals are slightly hygroscopic. They were kept in amber glass containers and remained white or nearly so for months.

The starting material for the preparation of barium selenite was commercial barium carbonate. This salt was dissolved in nitric acid and recrystallized several times. The purified nitrate was treated with a slight excess of selenious acid, and the selenite precipitated by gradual addition of ammonia, at the boiling point. The precipitate was washed free of ammonia and dried on filter paper, which seems to have no reducing action on it. Analysis of a typical lot: SeO₂, 41.96%, calcd. 41.99%; BaO, 58.19%, calcd. 58.01%. Through the courtesy of Mr. Paul Keene of the Solvay Process Co., a spectrogram was obtained, which indicated the presence of calcium, copper, aluminum, iron, and magnesium to an extent of much less than 0.1% in any case. Qualitative tests by the Noyes procedure also showed less than 0.1% of nitrate, ammonium, and carbonate ions. Samples of this material were preserved in colorless glass containers for over two years without showing reduction. The portion used for solubility measurement on the pure salt was extracted with water for several weeks in a Soxhlet apparatus.

For the preparation of barium pyroselenite, the normal selenite was digested with an excess of selenious acid at about 50° for several weeks, to ensure complete conversion. The crystals were drained by suction, washed thoroughly

(1) Berzelius, *J. Chem. Phys.*, **23**, 309 and 430 (1818), and elsewhere.

(2) Muspratt, *J. Chem. Soc.*, **2**, 52 (1850).

(3) Nilson, *Regiae Societatis Scientiarum Upsaliensis, Nova Acta*, [3] **9**, fasc. 2, II (1875).

(4) Boutzourcano, *Ann. chim. phys.*, [6] **18**, 309 (1889).

(5) Janitzki, *Z. anorg. allgem. Chem.*, **206**, 49 (1932).

(6) Janickis, *ibid.*, **218**, 89 (1934).

with water, and dried on a porous plate; analysis of a typical lot: SeO_2 , 59.34%, calcd. 59.16%; BaO , 40.70%, calcd. 40.84%. Samples were stored in colorless glass containers for over two years without showing reduction.

The analytical reagents were of the usual analyzed grade. A good grade of distilled water was used.

Temperature Regulation.—The solubility measurements were carried out in baths improvised from heavy glass battery jars. Those used at 0 and 50° were insulated with asbestos. The 0° bath was maintained at that temperature by the addition of chopped ice. The other baths were heated by electric light bulbs and held within $\pm 0.1^\circ$ of the nominal temperature by a thermo-regulator and vacuum tube control. The heated baths were agitated by streams of compressed air, so arranged as not to impinge upon the sample bottles, regulator, or thermometer.

Attainment of Equilibrium.—Attainment of equilibrium in those regions of concentration where the pyroselenite is the stable solid phase is much more rapid from undersaturation than from supersaturation. We have, therefore, ordinarily approached the equilibrium by starting with solid and water, although sufficient results from the supersaturated side were secured to confirm the attainment of saturation. Exploratory test-tube experiments over the whole field indicated the general form of the solubility curves and the location of the quadruple points. Weighed amounts of solids, slightly more than necessary to saturate the proposed quantity of solution, were introduced into the sample bottle and a measured volume of water added. The runs were made in amber glass bottles to avoid possible photochemical decomposition of the selenious acid. The bottles were sealed with wired-in corks, which were paraffined at the lower temperatures. The lower ends of the corks were covered with cellophane shields to prevent contamination of the solutions by fragments of cork or paraffin. The bottles were shaken by hand at frequent intervals. Saturation was obtained in one or two days with the more concentrated solutions, for which volumes of the order of only 5 or 10 ml. were employed, but over two weeks were required for saturation of about 500 ml. of water with normal selenite at 0°. In every case reported, consecutive samples, taken at intervals of three days to two weeks, gave concordant results. The maximum absolute deviations from the mean composition of saturated solutions, found upon analysis of consecutive samples, from the same complex or from parallel samples representing identical points on the diagram, were as follows: for barium selenite, 0.10% in a content of about 3.5% (this was exceptional); for total selenium dioxide, 0.25% in a content of about 75%.

Sampling and Analysis.—Samples were removed by pipets, warmed if necessary, through filters. The filters apparently have no significant reducing action on the selenious acid in the brief time of contact necessary. The samples were transferred to tared 100-ml. volumetric flasks, in which they were weighed on an analytical balance. They were then diluted to the mark with water, and appropriate portions were removed by pipet for analysis.

Barium was determined by precipitation as sulfate. The procedure recommended by Hillebrand and Lundell⁷

was followed. Under these conditions, there appears to be no significant interference from the selenite. Agreement of duplicate determinations upon the same sample was within the error of the weighings.

Total selenious acid was determined by the method of Norris and Fay⁸ as modified by Coleman and McCrosky.⁹ Numerous experiments by us support their findings. Samples were analyzed in triplicate, except for a few in which the selenium content was very small and a large volume of solution was necessary. Duplicate samples checked to within 0.10 to 0.20% in a content of about 75%.

The results were calculated in terms of free selenium dioxide, barium selenite, and water (by difference).

Solid Phases.—Portions of suspended solids were examined under the microscope, on heated or cooled slides when this was advisable, at each sampling period. The three solid phases encountered are readily distinguishable by their forms. The selenious acid crystals are well developed and usually rather large prisms. The pyroselenite crystals are needle-like, usually rather ragged. The normal selenite forms very small rhombs.

Some analyses were made to identify the phases by the Schreinemakers method, except in the case of the normal selenite, which is stable over too short a range of composition for accurate results to be obtained upon its degree of hydration. When analyzed, the wet residues were "blotted" as dry as possible with a filter, and dissolved in water or acid, the weight being obtained by difference. The details of the analysis were as previously described.

To establish identities in certain special cases, as discussed below, we have resorted to X-ray diffraction patterns, which were obtained by the powder method with a General Electric machine.

Results

The results on the system at the temperatures 0, 25, and 50° are given in Table I.

TABLE I

COMPOSITION OF SATURATED SOLUTION AND SOLID PHASE
Solid phases: A, selenious acid (H_2SeO_3); P, barium pyroselenite (BaSe_2O_6); N, barium selenite (BaSeO_3).

Free SeO_2 , %	Solution BaSeO_3 , %	Free SeO_2 , %	Wet solid BaSeO_3 , %	Identity of solid (by microscope)
At 0°				
58.9	0.00			A
58.8	1.24	73.8	0.35	A
58.7	2.51	77.1	.80	A
58.7	3.51	76.5	1.91	A + P
58.6	3.54	62.1	13.5	A + P
58.6	3.53	56.0	18.9	A + P
58.7	3.51	56.3	12.0	A + P
57.8	3.42	52.1	17.6	P
52.8	2.77			P
49.7	2.44			P
44.3	1.99			P
35.6	1.44	34.1	21.7	P
30.6	1.18			P
26.6	1.10			P

(8) Norris and Fay, *Am. Chem. J.*, **18**, 703 (1896).

(9) Coleman and McCrosky, *Ind. Eng. Chem., Anal. Ed.*, **9**, 431 (1937).

(7) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 504.

TABLE I (Concluded)

Solution		Wet solid		Identity of solid (by microscope)
Free SeO ₂ %	BaSeO ₃ %	Free SeO ₂ %	BaSeO ₃ %	
17.9	0.89	22.7	28.3	P
8.80	.69	19.9	37.0	P
4.57	.58	17.1	39.5	P
2.04	.58			P
1.11	.65			P
0.28	.64			P
.27	.64	6.9	38.5	P + N
.17	.39			N
.00	.005			N
At 25°				
68.8	0.00			A
68.3	1.54	79.7	0.50	A
67.7	3.13	79.2	1.05	A
67.3	4.61	77.9	2.09	A
67.2	5.03	75.7	3.44	A + P
67.1	5.12	74.6	4.14	A + P
67.2	5.04	69.2	8.62	A + P
63.6	4.36	57.2	14.6	P
59.9	3.84	55.9	13.1	P
44.7	2.42	38.8	29.5	P
33.2	1.74	32.4	21.9	P
23.3	1.33			P
13.5	1.09	22.6	41.1	P
5.94	0.97	17.0	35.7	P
1.27	.96	14.5	33.2	P
0.41	.95	18.0	43.4	P
.42	.97			P + N
.25	.58			N
.00	.005			N
At 50°				
76.6	0.00			A
76.2	1.51	81.8	0.59	A
75.4	2.75			A
74.8	3.66	81.1	1.55	A
73.8	5.80	80.2	2.58	A
73.5	6.67	79.1	4.44	A + P
73.4	6.59	77.0	4.18	A + P
71.8	6.42	67.2	12.3	P
68.3	5.32			P
57.8	3.90	51.8	15.6	P
44.7	2.81			P
37.1	2.38			P
24.7	1.80	24.6	24.0	P
13.7	1.45			P
4.87	1.28	14.7	29.7	P
1.34	1.16	12.0	27.5	P
0.51	1.18	9.7	24.7	P
.52	1.18			P + N
.29	0.67			N
.00	.005			N

These data are supported by a large number of results obtained during the earlier runs, but not listed here because the experimental conditions were not entirely satisfactory.

The results are shown graphically in Figs. 1, 2, and 3.

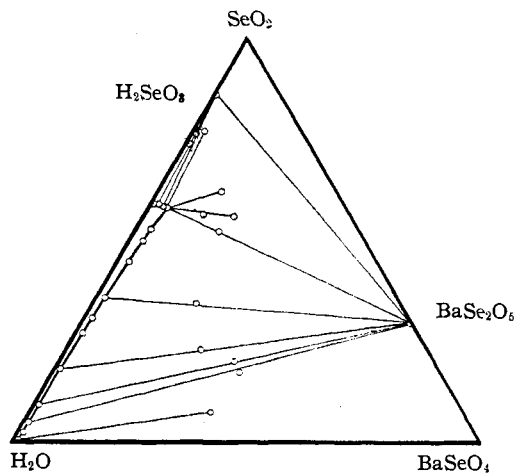


Fig. 1.—The system SeO₂-BaSeO₃-H₂O, at 0°.

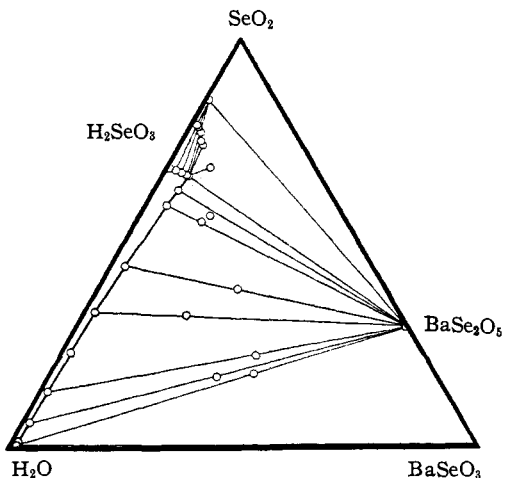


Fig. 2.—The system SeO₂-BaSeO₃-H₂O at 25°

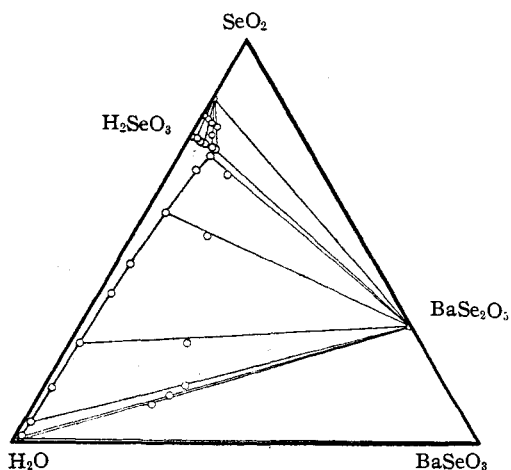


Fig. 3.—The system SeO₂-BaSeO₃-H₂O at 50°.

The following points deserve comment. The microscopic examination indicates that there is only a single modification of each solid

phase over the temperature range studied. This is in agreement with the results of Manchot and Ortner¹⁰ for selenious acid.

Berzelius¹ viewed the normal selenite of barium as anhydrous. Nilson,³ who prepared it by the rather extraordinary procedure of mixing solutions of barium nitrate and sodium biselenite, found it to be a monohydrate. We have attempted repeatedly to duplicate his work, but have obtained only the pyroselenite by this means, according to the X-ray diffraction pattern of the powdered material. We have also attempted to prepare the hydrate by precipitation of the normal selenite at 0° instead of the boiling point, but this yields the anhydrous salt, according to the diffraction pattern. Moreover, the anhy-

drous salt, even on exposure to water at 0° for several months, shows no change in form or appearance detectable under the microscope. We conclude that the hydrate, if it exists at all, is unstable above 0°.

The only previous data available as a check upon our solubility measurements are upon selenious acid alone. The summary is given in Table II. We are unable to suggest an explanation for the discrepancy.

Summary

1. Data on the solid-solution equilibrium have been obtained for the ternary system selenium dioxide-barium selenite-water at 0, 25, and 50°.

2. At each temperature the stable solid phases prove to be selenious acid, H₂SeO₃, barium pyroselenite, BaSe₂O₆, and barium selenite, BaSeO₃, all three of which have long been known.

3. No indication of hitherto unknown acid salts or hydrates has been found within the temperature range studied.

4. The normal salt monohydrate BaSeO₃·H₂O reported by Nilson cannot be confirmed.

SYRACUSE, N. Y.

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TABLE II

SUMMARY OF SOLUBILITY DETERMINATIONS ON SELENIOUS ACID

Investigators	% SeO ₃ in saturated solution at		
	0°	25°	50°
Étard ¹¹	47.3 ^a	66.7 ^a	78.2 ^a
Manchot and Ortner ¹⁰	65.9 ^a	73.3 ^a	79.2 ^a
Neal and McCrosky	58.9	68.8	76.6

^a Interpolated.

(10) Manchot and Ortner, *Z. anorg. allgem. Chem.*, **120**, 300 (1922).

(11) Étard, *Ann. chim. phys.*, [7] **2**, 551 (1894).

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

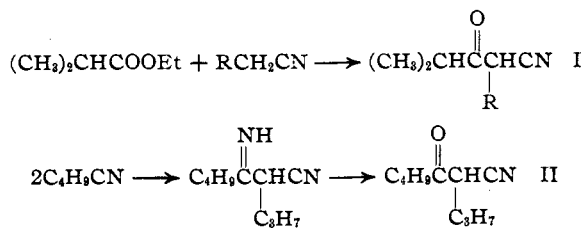
Reactions of β-Keto-nitriles with Hydrogen

BY RICHARD H. WILEY¹ AND HOMER ADKINS

Recent papers from this Laboratory on the reactions of hydrogen by Sauer, Durland, Musser and Mazingo have been concerned with the selective hydrogenation of compounds containing two functional groups, *i. e.*, unsaturated esters, amido esters, imido amides, polynuclear aromatic compounds and unsaturated ketones. Attention is now directed toward the selective hydrogenation of keto-nitriles over Raney nickel. Both the keto and cyano groups accept hydrogen under rather mild conditions with this catalyst; in fact some ketones and cyanides have reacted with hydrogen at room temperatures.² However, the preferred range of temperature for the hydrogenation of cyanides is 120–140°, which is somewhat above that ordinarily used for the hydrogenation of ketones. There has been no infor-

mation available, in so far as we know, with regard to which group over nickel would be hydrogenated first in the presence of the other.³

The keto-nitriles used in this investigation were prepared either by the condensation of an ester with a nitrile under the influence of sodium ethoxide, I, or through the condensation of two molecules of a cyanide by sodium followed by the hydrolysis of the imino nitrile, II.



(1) Wisconsin Alumni Research Foundation Fellow, 1935–1937.

(2) Adkins and Covert, *THIS JOURNAL*, **54**, 4116 (1932).

(3) A thesis at Leipzig by F. R. Urluss on the hydrogenation of keto-nitriles over palladium is listed for 1931.