

TABLE II

## DETERMINATIVE TABLE FOR IDENTIFICATIONS OF FIVE SUGARS BY OPTICAL EXAMINATION OF THEIR PHENYLOSAZONES

Observation	Sugar is
Immerse substance in liquid with $n = 1.730$	
Two $n$ 's (both crosswise) lower than liquid, = that of third	maltose
One $n$ (crosswise) lower than liquid, other two much greater	xylose
All $n$ 's much higher than liquid, then:	
Immerse substance in liquid with $n = 1.790$	
Two $n$ 's (both crosswise) much lower than liquid, third slightly higher	arabinose
One $n =$ liquid ( $\underline{30}^\circ$ with elongation), others higher	galactose
Two $n$ 's less and one much greater, elongation $\neq$	glucose

WOOSTER, OHIO

## NOTES

## The Existence of the High-Temperature Form of Cristobalite at Room Temperature and the Crystallinity of Opal

BY J. W. GREIG

There has appeared recently an interesting letter from Levin and Ott<sup>1</sup> announcing that they have established, by means of x-rays, the existence of the high-temperature modification of cristobalite in a number of opals. So far as I am aware, the high-temperature modification of cristobalite has not before been shown to occur in nature at atmospheric temperatures. In my opinion, however, this form has, contrary to their statement, been shown to be present at room temperature in certain artificial products.

In the course of experimental determinations of points on the liquidus of silica, in systems of silica with other oxides, carried out at this Laboratory, study of the charges frequently shows that some of the cristobalite crystals embedded in the glass are sensibly isotropic, often in contrast to other birefringent ones in the same melt. This has been observed repeatedly by microscopists doing this work here and was explained by Andersen as due to some of the crystals of cristobalite failing to invert during cooling and so persisting in the high-temperature cubic modification.<sup>2</sup>

In connection with a study of the decomposition of cyanite,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , at high temperatures to give mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and silica, I have investigated the question of the form in which the silica was present in the product of decomposition.<sup>3</sup> When first formed the products of the decomposition are so fine-grained that some question remains as to the nature of the silica, but with continued heating at high temperature it collects

<sup>1</sup> Levin and Ott, *THIS JOURNAL*, **54**, 828 (1932).<sup>2</sup> O. Andersen, *Am. J. Sci.*, **39**, 418 (1915).<sup>3</sup> J. W. Greig, *J. Am. Ceram. Soc.*, **8**, 478-481 (1925); *Am. J. Sci.*, **11**, 21-25 (1926).

into larger particles and is then definitely cristobalite. On cooling through the inversion temperature the cristobalite remains, as indicated by thermal studies, for the most part in the high-temperature form.

Although they do not explicitly say so, Levin and Ott have evidently based their opinion, that the high-temperature form of cristobalite has not before been shown to exist at room temperature, on the fact that Sosman, in his monograph on silica,<sup>4</sup> mentions only two reports to that effect and discusses both unfavorably. It is to be noted that the experiments described in these reports are of a somewhat different nature from those mentioned in the preceding paragraphs. In both these cases the cristobalite was already in the low-temperature form and supposedly free from any enclosing solid medium. As will appear later, this is probably an important difference. Sosman's remarks, quoted from p. 133, follow.

"Endell stated in 1912 that he had found the low-to-high inversion of cristobalite to be reversible with difficulty, and that rapid cooling after the crystals had been heated to above 220° left them in the isotropic high-form, from which the change" [to the low-temperature birefringent form] "at atmospheric temperature was a matter of some hours" (phrase in brackets mine).

"Schwarz has also stated that cristobalite after being heated about 15 minutes at 250° and then quickly cooled remains isotropic.

"These statements are in such direct contradiction to the numerous observations of all other investigators that it can hardly be admitted without further evidence that the phenomena observed were really due to a delayed inversion. It is easy to be mistaken on this point because cristobalite after passing through the inversion is very fine grained, and its birefringence, furthermore, is small, so that it may give a false appearance of being isotropic."

One must agree with Sosman that more evidence is needed before one can accept their conclusions as established, for their reported results are not in accord with general experience with cristobalite. The two forms of cristobalite are distinguishable by other properties than birefringence, yet no one, so far as I am aware, has since reported the same result, although many experimenters have studied cristobalite since 1912. It must, however, be noted that Sosman's suggested explanation cannot account for Endell's reported observations. It could indeed explain only the first part and would put anyone accepting it in a difficult position in respect to the second part. If one accepts it he must, to explain the reappearance at room temperature of the normal birefringent aspect, assume further that in this aggregate of cristobalite, already in the low-temperature form, individual crystals grew markedly in a few hours at room temperature.

<sup>4</sup> R. B. Sosman, "The Properties of Silica," American Chemical Society Monograph 37, 1927.

It is appropriate here to mention two additional sets of observations, so far unpublished, indicating that under certain conditions the high-temperature form of cristobalite may be brought to room temperature without inverting. The first of these is a confirmation of Andersen's opinion. I have examined literally hundreds of charges, similar to those described by Andersen, in which well-formed cristobalite crystals occur distributed in glass. It is quite normal to find, using crossed nicols, that sensibly isotropic cristobalite crystals as well as birefringent cristobalite crystals occur together in the same preparation. Since the inversion from the high-temperature to the low-temperature form is accompanied by a considerable decrease in volume, the high-temperature isotropic form should have the lower index of refraction. It should thus be possible, by this property, to differentiate them readily, if they were embedded in a medium with an intermediate index of refraction. In order to apply this test I have prepared suitable glasses with indices of refraction lower than those of the low-temperature form (*i. e.*,  $n < 1.485$ ), and, by holding these at a temperature immediately under that of the cristobalite liquidus, have grown excellent faceted crystals of cristobalite in them. The cristobalite crystals in these glasses after cooling to room temperature were of both the isotropic and the birefringent kinds. The isotropic crystals had always a low index of refraction (not far from that of a glass  $n = 1.46_6$ ), and were thus definitely differentiated from those that had inverted and that had therefore a higher index of refraction than the glass. Reëxamination of some of these preparations after they had stood for over three years at room temperature showed that sensibly isotropic crystals with this low index of refraction were still present. It is accordingly concluded that in these glasses cristobalite in the high-temperature form may be cooled to room temperature without inverting and will there remain in that form for an indefinite time.

In the case of certain silicate liquids it is extremely difficult to prevent the crystallization of cristobalite during cooling. When such liquids are chilled the cristobalite appears as small crystals thickly distributed throughout so that the quenched products vary, depending on the size and number of the crystals, from faintly opalescent to porcelain-like.<sup>5</sup> I have made heating and cooling curves on several such porcelain-like "glasses" using a differential apparatus sufficiently sensitive to detect the heat absorption or evolution accompanying the inversion of a fraction of the cristobalite present, yet these curves showed no trace of such heat effect. The cristobalite in them did not invert sharply on cooling through the inversion temperature.

In the cases that I have described, from my own experience, in which high-temperature cristobalite was cooled through the inversion tem-

<sup>5</sup> J. W. Greig, *Am. J. Sci.*, **13**, 40-44 (1927).

perature without inverting, the crystals were small and embedded in some solid medium: in one case intergrown with mullite crystals, in the other cases embedded in a siliceous glass. In the glasses with an index of refraction  $< 1.485$  mentioned above the glass immediately surrounding the crystals with the low index of refraction is, at room temperature, invariably birefringent, showing that it is strained. The relation of the vibration directions of the fast and slow rays in the strained glass to the enclosed crystal, together with the localization of the strain, indicate that the strain is due to a contraction of the crystal that is being resisted by the glass. The glass and crystal are therefore adhering. This strain fades out on heating but on cooling reappears, becoming evident at a temperature somewhat above that of the inversion, and increasing as the temperature is lowered. The glass surrounding the crystals that have inverted to the low-temperature form, on the other hand, is not strained, and in some cases it is even possible by careful microscopic work to see that a crack surrounds the crystal. The inversion and the breaking free of the crystal from the restraint of the glass are thus associated. Such crystals invert to the high-temperature form on heating and back again on cooling, as may readily be seen by watching them under the microscope during the process. It is probable, in view of the strong contrast between the behavior of the crystals mechanically attached to the surrounding glass and that of free crystals, whether surrounded by the glass as these are, or prepared by some other method and entirely separate, that the solid embedding medium exercises an important restraint on the inversion of the attached crystals.

Since the appearance of the letter by Levin and Ott, Dr. E. Posnjak has obtained an x-ray spectrogram, corresponding closely to that given by the high-temperature form of cristobalite, from a translucent amber-colored "resin opal" from Queretaro, Mexico. Dr. H. E. Merwin and I have examined this material under the microscope. It is then resolved into two parts, a matrix  $n = 1.41$  and, thickly distributed through it, small particles of considerably higher index of refraction. In all likelihood these particles are the crystals giving rise to the x-ray pattern. If, as seems most probable, they are indeed the high-temperature form of cristobalite, they are probably another example of small crystals of cristobalite embedded in a medium failing to invert on cooling through the inversion temperature, for, on the basis of our present very limited knowledge, this is considered more probable than that the high-temperature form of cristobalite would crystallize in the temperature range in which the low-temperature form is the more stable.

## The Preservation and Determination of Sodium Sulfo cyanate

BY JOSEPH GREENSPAN

Several recent improvements in the analytical determination of thiocyanates by oxidation with iodine in appropriate alkaline buffers permit of a more precise investigation of the kinetics of reactions involving thiocyanate ion.<sup>1</sup> In searching the literature for means of preventing mold formation in standard aqueous solutions of sodium thiocyanate, we were struck by the paucity of information regarding this salt.<sup>2</sup> We have found the following methods satisfactory.

**Preservation.**—The commercial c. p. salt was recrystallized from 95% alcohol. The addition of one drop of toluene per 100 cc. of approximately 0.02 *M* solutions completely prevented mold growth and loss of titer for a period of at least three weeks, whereas mold growth developed in the absence of toluene. Titration after two weeks of standing with toluene preservative gave a value of 0.01982 *M*; after three weeks, 0.01982 *M*.

**Analytical.**—The ammonia-ammonium salt buffer recommended by Pagel and Koch<sup>3</sup> developed iodine absorption after standing for several days, giving titer values of 13.38, 17.68, 15.92 cc. against the calculated 20.83, 20.64, 20.54 cc., respectively, although accurately concordant results were obtained with fresh buffer, giving 18.71, 20.43 cc. *vs.* calculated 18.67, 20.46 cc. The authors mention that traces of nickel, cobalt and manganese produce erratic results. Our solutions were kept in Non-Sol bottles.

Schwicker's<sup>4</sup> ammonium borate buffer method, as modified by Pagel and Ames,<sup>5</sup> yielded a black precipitate, presumably an iodide of nitrogen, which disappeared upon subsequent acidification. This method was therefore rejected in favor of that employing a borax buffer,<sup>5</sup> which yielded accurate and consistent values, 40.51, 40.53 cc. *vs.* calculated 40.49, 40.51 cc.

<sup>1</sup> See La Mer and Greenspan, *THIS JOURNAL*, **54**, 2739 (1932).

<sup>2</sup> Beilstein, 4th ed., Vol. III, p. 150; *Erstes Ergänzungswerk*, Vol. III, p. 66.

<sup>3</sup> Pagel and Koch, *THIS JOURNAL*, **53**, 1774 (1931).

<sup>4</sup> Schwicker, *Z. anal. Chem.*, **77**, 278-280 (1929).

<sup>5</sup> Pagel and Ames, *THIS JOURNAL*, **52**, 2698 (1930).

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DEPARTMENT OF CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK, N. Y.

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## The Equilibrium of Para and Ortho Hydrogen

BY ROY W. HARKNESS AND W. EDWARDS DEMING

Investigators in several laboratories are studying the transition of para to ortho hydrogen. In most of this work it is desirable to know the equilibrium ratio at different temperatures. There appears to be no accessible tabulation of this ratio, and it seems desirable to publish a table calculated

from Dennison's<sup>1</sup> equation, covering the range 20 to 273°K. Between these temperatures the equilibrium mixture changes from 99.82% para to 25.13%. In the accompanying table we give the ratio of para to ortho hydrogen and the percentage amount of para hydrogen at a sufficient number of temperatures for ordinary purposes. In the liquid air range values are given at every degree.

RATIO AND PERCENTAGE OF PARA HYDROGEN IN AN EQUILIBRIUM MIXTURE AT VARIOUS TEMPERATURES, CALCULATED FROM THE EQUATION

T, °K.	Ratio para:ortho	Para hydrogen, %	T, °K.	Ratio para:ortho	Para hydrogen, %	T, °K.	Ratio para:ortho	Para hydrogen, %
20	544.8	99.82	76	1.046	51.13	95	0.6801	40.48
21	363.5	99.73	77	1.017	50.41	100	.6262	38.51
22	251.6	99.60	78	0.9894	49.73	105	.5829	36.82
23	179.8	99.45	79	.9626	49.05	110	.5456	35.30
24	132.2	99.25	80	.9377	48.39	115	.5152	34.00
25	99.57	99.01	81	.9140	47.75	120	.4897	32.87
30	32.07	96.98	82	.8916	47.13	130	.4498	31.03
35	14.28	93.45	83	.8702	46.53	140	.4208	29.62
40	7.780	88.61	84	.8500	45.95	150	.3994	28.54
45	4.853	82.91	85	.8307	45.37	160	.3835	27.72
50	3.327	76.89	86	.8123	44.82	170	.3715	27.09
55	2.443	70.96	87	.7981	44.39	190	.3555	26.23
60	1.890	65.39	88	.7781	43.76	210	.3463	25.72
65	1.521	60.33	89	.7621	43.25	230	.3409	25.42
70	1.264	55.83	90	.7469	42.75	250	.3377	25.24
75	1.077	51.86	91	.7323	42.27	273	.3357	25.13

The ratio of para to ortho hydrogen, as given by Dennison, is

$$\frac{1 + 5e^{-6x} + 9e^{-20x} + 13e^{-42x} + \dots}{9e^{-2x} + 21e^{-12x} + 48e^{-30x} + \dots}$$

wherein  $x = h^2/8\pi^2 JkT$ . We have adopted the following values, in C. G. S. units:  $h = 6.547 \times 10^{-27}$ ,  $k = 1.371 \times 10^{-16}$ ,  $J = 0.466 \times 10^{-40}$ , so that  $xT = 84.977$ .  $J$  is the moment of inertia of the hydrogen molecule, and the value  $(0.466 \pm 0.001) 10^{-40}$  was estimated by Birge and Jeppesen.<sup>2</sup> Increasing  $J$  by  $0.001 \times 10^{-40}$  lowers the calculated percentage of para hydrogen 0.13 per cent. in the central portion of the curve and much less at the end portions. The series in the numerator and denominator converge rapidly over the temperature range used; the expression written above contains all the terms needed for the accuracy of the accompanying table.

Eucken and Hiller<sup>3</sup> published six values of the ratio para : ortho hydrogen, at  $T = 21.2, 28.3, 42.5, 60.0, 85, 170$ , which agree with the entries in our table except at their two highest temperatures,  $T = 85$  and  $170^\circ$ .

<sup>1</sup> D. M. Dennison, *Proc. Roy. Soc. (London)*, A115, 483 (1927).

<sup>2</sup> R. T. Birge and C. R. Jeppesen, *Nature*, 125, 463 (1930).

<sup>3</sup> Eucken and Hiller, *Z. physik. Chem.*, B4, 142 (1929).

At  $T = 85^\circ$  they give 48.0%, whereas we find 45.4; at  $T = 170^\circ$  they give 25.3, whereas we find 27.1. They presumably calculated their values

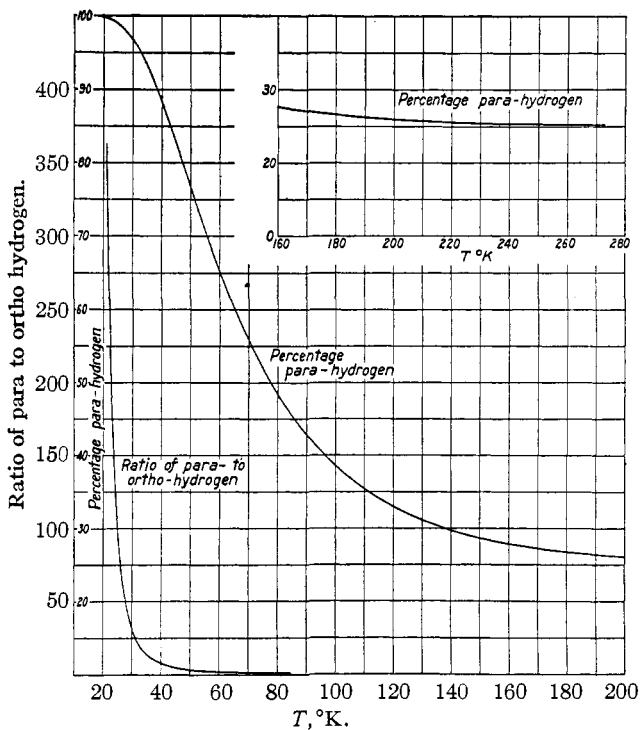


Fig. 1.

from Dennison's equation. We know of no explanation for this discrepancy. They used  $0.467 \times 10^{-40}$  for  $J$ , so it is not to be found there.

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BUREAU OF CHEMISTRY AND SOILS  
WASHINGTON, D. C.

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