

## 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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## The Equilibrium of Para and Ortho Hydrogen

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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

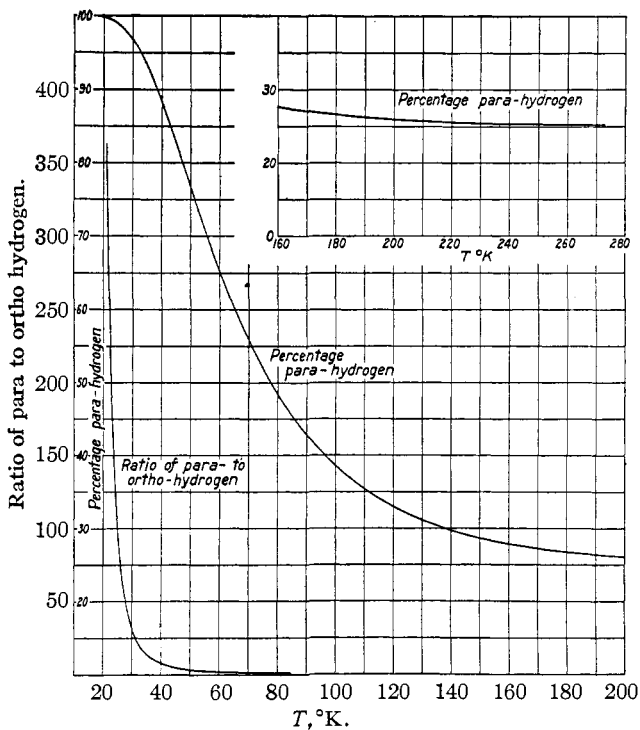


Fig. 1.

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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