# NOTES

## The Preparation of Selenic Acid

By L. I. Gilbertson and G. B. King

Selenic acid is commonly prepared by the method of Morris.[1] The method involves the precipitation of silver selenite and subsequent oxidation of this salt to selenic acid by bromine in aqueous solution. Unoxidized selenious acid is removed with hydrogen sulfide. Dennis and Koller[2] report that some selenic acid is reduced in the latter reaction with resultant contamination of the product. Moreover, the method is tedious, and inasmuch as relatively large amounts of silver salts are involved it is not well suited to large scale production.

The oxidation of selenious acid with hydrogen peroxide has received some attention. Partial oxidation has been reported by Meyer and Heider[3] and Huff and McCrosky.[4] It is the purpose of this paper to describe a method for the production of relatively large amounts of selenic acid using hydrogen peroxide as the oxidizing agent.

### Experimental

**Preparation of Materials.**—Selenium dioxide was prepared by oxidizing the commercial grade of powdered selenium with nitric acid. The product was purified by sublimation.

Hydrogen peroxide was the 100 volume, 30% product "Albone C."[5]

**Procedure.**—One hundred and fifty grams of resublimed selenium dioxide is added to 500 g. of 30% hydrogen peroxide in a 1-liter flask and allowed to stand for twenty-four hours. The mixture is then refluxed in an all-glass apparatus for twelve hours. Oxygen is bubbled through the solution during the refluxing to produce thorough agitation and to maintain an oxidizing atmosphere. A small portion is then withdrawn and is tested for the presence of selenious acid with a solution of sulfur dioxide in water. The test sample is discarded. If selenious acid is shown to be present, more hydrogen peroxide is added and refluxing is continued until oxidation is complete. Any undecomposed hydrogen peroxide and most of the water are removed by distillation on a steam-bath under reduced pressure (water aspirator). Remaining traces of moisture are removed by passage through the solution of a slow stream of dried air (over phosphorus pentoxide) at a temperature of 150–160° and a pressure of 4–6 mm. Higher temperatures than 160° are to be avoided to prevent thermal decomposition of selenic acid. The remaining viscous liquid has a specific gravity of approximately 2.6. The yield of selenic acid is 192–195 g.

The crystalline acid may be obtained readily by seeding the liquid at room temperature in a dry atmosphere. Solid selenic acid for seeding purposes may be obtained by cooling a small portion of the liquid with solid carbon dioxide. Crystallization takes place rapidly with the formation of long needle-shaped crystals which are very deliquescent. The acid is effectively dried by pumping dry air over the crystals for several days at low pressure. The resulting product gives a freezing point of 55–56°, and analyzes 99.8% selenic acid.

CONTRIBUTION FROM THE
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(1) Morris, *Trans. Wisconsin Acad. Sci.*, **19**, 369 (1918).

(2) Dennis and Koller, This Journal, **41**, 949 (1919).

(3) Meyer and Heider, *Ber.*, **48**, 1154 (1915).

(4) Huff and McCrosky, This Journal, **51**, 1457 (1929).

(5) Hydrogen peroxide was kindly furnished by E. I. du Pont de Nemours and Company, Incorporated.

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## Equation for Approximating Heat Capacities of Gases Calculated from Spectroscopic Data

By I. N. Godnev

In order to approximate the heat capacities of gases calculated from spectroscopic data Spencer and Justice[1] recently applied in the range 300–1500°K. the equation

$$C_p = a + bT + cT^2 \qquad (1)$$

The failure of equations of this type to represent actual heat content data[2] forced Chipman and Fontana[3] to propose the following expression for heat capacities of solids and gases

$$C_p = a + bT + cT^{-1/2} \qquad (2)$$

The latter authors have shown that this equation is applicable to heat capacities of gases calculated from spectroscopic data up to 2000°K.

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(1) Spencer and Justice, This Journal, **56**, 2311 (1934).

(2) Maier and Kelley, *ibid.*, **54**, 3243 (1932).

(3) Chipman and Fontana, *ibid.*, **57**, 48 (1935).

It is evident that it will be useful to find the approximate equation for heat capacities of gases available for a wider interval of temperatures. We present here a solution of this problem.

For this purpose let us take the expression

$$\alpha = C_p - C'_p \qquad (3)$$

where $C_p$ is the exact molecular heat capacity and $C'_p$ is that calculated by means of the equation of the Planck–Einstein type[4]

$$C'_p = C_{p_0} + \Sigma\varphi(\Theta_\kappa/T) \qquad (4)$$

Our calculations have shown that $\alpha$ increases with the increase of temperature. In many cases this value is proportional to temperature $T$. We may approximate

$$\alpha = aT + bT^2 \qquad (5)$$

From equations (3), (4) and (5) it follows

$$C_p = C_{p_0} + \Sigma\varphi(\Theta_\kappa/T) + aT + bT^2 \qquad (6)$$

This equation, as has been shown by our calculations, may be used for approximating heat capacities of gases calculated from spectroscopic data in a wide range of temperatures. The application of the equation (6) is not cumbersome, as good tables of the Planck–Einstein functions have been available and almost anyone can read off $C_p$ in a few minutes. The applicability of the equation (6) was examined by us for nitrogen, carbon monoxide and sulfur. Using the data of Johnston and Davis[5] we have derived the following equations for nitrogen and carbon monoxide

$$N_2\colon C_p = 7/2R + \varphi(3360/T) + 0.40\cdot10^{-4}T \qquad (7)$$

$$CO\colon C_p = 7/2R + \varphi(3090/T) + 0.40\cdot10^{-4}T \qquad (8)$$

where $\varphi$ represents Planck–Einstein function for two degrees of freedom. The coefficient $b$ in both cases may be taken equal to zero.

The heat capacities calculated from these expressions agreed over the range of 50–5000°K. with an average deviation of ± less than 0.1% and with a maximum deviation of less than 0.3%.

In case of sulfur vapor, $S_2$, the application of the equation (6) gives the expression

$$C_p = 7/2R + \varphi(1042/T) + 0.60\cdot10^{-4}T \qquad (9)$$

the coefficients of which we have obtained from the spectroscopic calculations of Godnev and Sverdlin.[6] The value $\Theta$ is taken from our latter data.[7]

Equation (9) fits the theoretical molecular heat capacity curve in the interval 100–5000°K., with an average deviation of less than 0.1% and with a maximum deviation of 0.2%.

## Summary

An equation is proposed for the approximate representation of the heat capacities of gases calculated from spectroscopic data

$$C_p = C_{p_0} + \Sigma\varphi(\Theta_\kappa/T) + aT + bT^2$$

the applicability of which was examined for carbon monoxide, nitrogen and sulfur in the range 100–5000°K.

In these cases the approximation may be carried out very well with the coefficient $b$ equal to the zero for the temperature interval 100–5000°K.

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[4] Bryant, *Ind. Eng. Chem.*, **25**, 820 (1933).

[5] Johnston and Davis, THIS JOURNAL, **56**, 271 (1934).

[6] Godnev and Sverdlin, *J. Exp. Theoret. Physics* (U. S. S. R.), **5**, 864 (1935); *Z. Physik.*, **97**, 124 (1935).

[7] Godnev, *Phys. Z. Sow. Un.*, **7**, 442 (1935).

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## 2,6-Dimethylphenyl α-Naphthylcarbamate

BY CHARLES D. HURD AND M. A. POLLACK

Phenol and a xylenol were among the pyrolytic products of furfural.[1] Because of its melting point, 46°, the xylenol was thought to be 2,6-dimethylphenol. Its α-naphthyl isocyanate derivative melted at 174–175° but this was an unknown derivative at the time. In the present note this deficiency is supplied and the xylenol definitely confirmed as 2,6-dimethylphenol. 2,6-Dimethylphenyl α-naphthylcarbamate, synthesized from authentic 2,6-dimethylphenol, was found to melt at 176.5°.

Eastman 2,6-dimethylphenol was used. It melted at 44° and underwent smooth bromination to yield 3,4,5-tribromo-2,6-dimethylphenol,[2] m. p. 201° (from petroleum ether).

One gram of the dimethylphenol and 1 g. of α-naphthyl isocyanate were mixed in a test-tube. When one drop of a solution of trimethylamine in dry ether was added, an exothermic reaction set in and the contents of the tube solidified. The solid was crystallized from petroleum ether; m. p. 176.5°. The melting point was unchanged by crystallizing from alcohol, but beautiful white flakes were formed thereby; yield, 1.7 g.

*Anal.* (By Howard Pollack). Calcd. for $C_{19}H_{17}O_2N$: C, 78.32; H, 5.88. Found: C, 78.47; H, 6.00.

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[1] Hurd, Goldsby and Osborne, THIS JOURNAL, **54**, 2536 (1932).

[2] Auwers and Markovits [*Ber.*, **41**, 2336 (1908)] record the m. p. of 200–201°.