

Note on the Third Law Calculation of the Entropy and Free Energy of Ammonia.—A calculation of the molecular entropy and free energy of formation of ammonia has been made by means of the third law of thermodynamics using the low temperature heat capacity data of this compound. The calculated molecular entropy and free energy of formation are, respectively, 46.7 entropy units, and -4150 calories at 298.1°K .

There has been considerable uncertainty regarding the proper value of the entropy of hydrogen to be used in thermodynamic calculations in combination with other molecular entropies obtained by means of the third law. For this purpose, Giauque¹ has recommended a value derived from the absolute entropy of ordinary hydrogen obtained from spectral data, modified by the principle of nuclear spin cancellation.² This value has been found satisfactory for systems of monatomic and diatomic substances, but has not been conclusively tested for larger molecules. Since the thermal data and equilibrium in the ammonia synthesis, $\frac{1}{2}\text{N}_2(\text{g}) + 1\frac{1}{2}\text{H}_2(\text{g}) = \text{NH}_3(\text{g})$, are known with a high order of precision,³ and since there are now sufficient measurements upon ammonia at low temperatures to permit a calculation of the molecular entropy, this substance serves as a test of the applicability of the third law, and more particularly of Giauque's value for the entropy of hydrogen.

The low temperature heat capacity measurements used in the present calculation are those of Clusius, Hiller and Vaughen,⁴ also Eucken and Karwat.⁵ Heats of vaporization and fusion were taken from the work of Eucken and Donath.⁶ Extrapolation to 0°K . was carried out by the Debye function with $\theta = 215$. For the heat capacity of the gas, the values of Osborne⁷ and associates were used. The molecular entropy thus obtained is 46.7 entropy units at 298.1°K .

Assuming Giauque's value of 31.23 for the entropy of hydrogen, and 45.6 for that of nitrogen,⁸ the entropy change accompanying the formation of ammonia is -22.9 E. U. The heat of formation, $\Delta H_{298.1}$, which is equal to $-10,985$ calories, is obtained from Lewis and Randall's equation⁸

$$\Delta H = -9500 - 4.96T - 0.000575T^2 + 0.0000017T^3$$

The free energy of the ammonia synthesis can be derived from the above results by means of the second law, and is found to be: $\Delta F_{298.1}^\circ = -4150$,

¹ Giauque, *THIS JOURNAL*, **52**, 4816 (1930).

² Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 556-557.

⁴ Clusius, Hiller and Vaughen, *Z. physik. Chem.*, **8B**, 427 (1930).

⁵ Eucken and Karwat, *ibid.*, **112**, 467 (1924).

⁶ Eucken and Donath, *ibid.*, **124**, 181 (1926).

⁷ Osborne, Stimson, Sligh and Cragoe, Bur. Standards Sci. Paper No. 501, Washington, D. C., 1925.

⁸ Lewis and Randall, Ref. 3, p. 464.

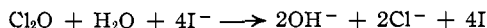
which may be compared with the experimental $\Delta F_{298.1}^{\circ} = -3910$ given by Lewis and Randall.⁸ If the previously accepted value⁹ of 29.6 for the entropy of hydrogen be used instead of that later recommended by Giauque,¹ $\Delta F_{298.1}^{\circ} = -4900$ is obtained. It is obvious that Giauque's value gives the better agreement with experiment.

Villars¹⁰ has calculated the molecular entropy of ammonia from spectroscopic data. His figure, 44.0 E. U., is not given on the same basis as the above value. When Villars' result is made comparable with the entropy of hydrogen used here (31.23), his value becomes 46.5, in close agreement with the 46.7 given above.

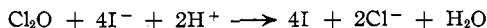
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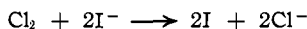
The Analysis of Chlorine Monoxide-Chlorine Mixtures.—Chlorine monoxide may be determined by absorption in potassium iodide solution and titration of the iodine liberated.



It is necessary to acidify the solution before titrating with thiosulfate.¹



The liberation of OH^- provides a further means for the determination of chlorine monoxide and indicates a method for the analysis of chlorine monoxide-chlorine mixtures.



Excess of standard sulfuric acid is added and after titration of the total iodine with thiosulfate the excess acid is found by back titration with standard alkali. Bowen² used methyl orange as indicator, while Hinshelwood³ used *N*/10 baryta and phenolphthalein. If x cc. of thiosulfate is used and then y cc. of sulfuric acid is required to neutralize the OH^- ; $\text{Cl}_2\text{O} \propto y$ and $\text{Cl}_2 \propto x - 2y$. Acid, base and thiosulfate must all be of the same normality or correcting factors are necessary.

The analysis can be simplified by an adaptation of the method used by Bodenstein⁴ for the analysis of chlorine-ozone mixtures.

As before, the gases are absorbed in potassium iodide solution and excess standard *N*/10 sulfuric acid added and the total iodine found.

⁹ Giauque and Wiebe, *THIS JOURNAL*, **50**, 121 (1928).

¹⁰ Villars, *ibid.*, **53**, 2006 (1931).

¹ Kistiakowsky, *Z. physik. Chem.*, **116**, 371 (1925).

² Bowen, *J. Chem. Soc.*, **123**, 1203 (1923).

³ Hinshelwood, *Proc. Roy. Soc. (London)*, **A131**, 177 (1931).

⁴ Bodenstein, Schumacher and Padelt, *Z. physik. Chem.*, **5B**, 209 (1929).