



DEPARTMENT OF ORGANIC CHEMISTRY
THE UNIVERSITY OF SYDNEY
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FRANCIS LIONS

THE CRYSTAL FORM OF NICKEL OXIDES

Sir:

In making adsorption measurements of carbon dioxide on nickel oxide, it was found by one of us¹ that the adsorptive properties of the oxide varied quite markedly for different modes of heat treatment.

The nickel oxide was prepared by oxidation of suspended nickelous hydroxide with chlorine gas in basic solution. The black precipitate of the oxide was electrolyzed free of alkali and dried. One sample was out-gassed several times at 285°, while the other was not subjected to a temperature of more than 110°.

The first preparation was the poorer adsorbent for carbon dioxide. The adsorption was carried out at 56.5° and the amounts adsorbed were in the approximate ratio of 1:2.5.

This difference of behavior, which was unlikely due to sintering, since the overheated form had rather smaller particle size as indicated by the line-width of the x-ray diagrams referred to below, also could not be explained on the basis of chemical differences, since in the Bunsen test for higher oxides, only traces of such could be found in either case. Both samples corresponded to nickelous oxide.

The substances were then subjected to x-ray analysis by means of the Debye-Scherrer-Hull method.

The overheated oxide corresponded exactly to the previously reported structure for nickelous oxide, being face-centered cubic. The edge of the unit cube was found to be 4.14 Å. (uncorrected), which corresponds to 4.17 Å. as given by the "International Critical Tables."

The structure of the nickelous oxide which had not been heated above 110° was quite different. Although also cubic, the edge of the unit cube was 4.64 Å. (uncorrected). The density was determined as 4.8 as compared to 6.69, given as the density of the ordinary nickelous oxide (Landolt-Börnstein "Tabellen"). The number of molecules in the unit cell

¹ O. G. Bennett, "Thesis," The Johns Hopkins University, 1930.

was calculated as four, with the same accuracy as for the known oxide. However, from a consideration of the intensities of reflection, the face-centered cubic type is not permissible. The complete determination of the atomic coordinates has not been finished as yet.

This form also differs from the ordinary nickelous oxide by causing an unusual amount of fogging on the photographic film when a Debye-Scherrer diagram is taken (Fe-radiation).

Evidently we have found a new cubic modification of nickelous oxide; we have also some evidence for the existence of further modifications. The possibility of the existence of several modifications of nickelous oxide is indicated by the work of Hedvall [*Z. anorg. Chem.*, **92**, 381 (1915)].

This work is being continued and special emphasis is laid on the determination of a possible relation between adsorption, catalysis and structure.

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O. G. BENNETT
R. W. CAIRNS
EMIL OTT

THE FREE ENERGY OF FORMATION OF THALLIUM AMALGAMS

Sir:

Recently Tammann has reviewed the subject of heterogeneous equilibria both from the theoretical and the practical standpoint.¹ Besides describing the different types of phase diagrams, he shows how they can be derived from purely thermodynamic considerations, using the surfaces in free energy (F)-temperature-composition space taken for the several phases. Successive isothermal planes cut the F -surfaces in curves which define the singular points on isothermal lines across the phase diagram.

These surfaces, however, give only form and characteristics of the general types of diagrams, and have not been applied to any specific systems, since absolute values of F , which are needed for the calculation, have not been obtained, although changes of the free energy are easily measurable.

Nevertheless I believe I have succeeded in calculating a curve for the system thallium-mercury which represents the general form of the intersection of the free energy surfaces for that system with the 20° isothermal plane. I have calculated the free energy of formation of thallium amalgams from the elements, using the data of Richards and Daniels,² Lewis and Randall,³ and Richards and Smyth⁴ by a method which I will explain

¹ Tammann, "The States of Aggregation," translated by Mehl, D. Van Nostrand Co., New York, 1925; Tammann, "Metallography," translated by Dean and Swenson, The Chemical Catalog Co., New York, 1925; Tammann, "Lehrbuch der Heterogenen Gleichgewichte," Vieweg and Son, 1924.

² Richards and Daniels, *THIS JOURNAL*, **41**, 1732 (1919).

³ Lewis and Randall, *ibid.*, **43**, 233 (1921).

⁴ Richards and Smyth, *ibid.*, **44**, 524 (1922).