

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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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).

in detail in the full report. Briefly, the free energy of formation is a linear function of the mole fractions and partial molal free energies of thallium and mercury in amalgamated and free states. If the last-named quantities—partial molal free energies of solid thallium and liquid mercury—were known, the true F -curve could be drawn; they are, however, constants at any given temperature, and enter my equations as products by the first power of the mole fraction, hence the only effect on the F -curve is to subject it to that type of linear transformation known as a "shear." While a "shear" will change certain features of a curve, such as slope, certain other features, in this case more important, are unchanged. The curve is presented (Fig. 1).

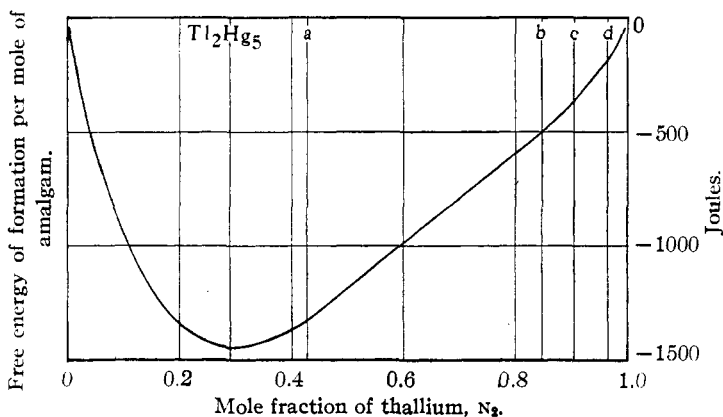


Fig. 1.—Free energies of formation of thallium amalgams.

The parts of the curve included between the vertical lines a and b , and c and d are straight lines, and will remain straight lines after a shear. Straight lines are to be expected, representing the common tangent to the free energy curves of the two phases in equilibrium in these regions. There is also a minimum at $N_2 = 0.285$ which is not to be expected from Tamman's treatment. It coincides, however, with the composition of the known compound Tl_2Hg_5 . The appearance of this minimum is all the more surprising since no singular point appears in the e. m. f. curve at this composition, and 20° is five degrees above the melting point of the compound, so that we have it existing in solution only.

Complete details of the method and calculations will be presented in an article to be submitted shortly.

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