CaF$_2$(α): $H_T - H_{298.16} = 14.30T + 0.00364T^2 - (46,900/T) - 4430$ (298 — 1424°K; 0.3%)

CaF$_2$(β): $H_T - H_{298.16} = 25.81T + 0.00125T^2 - 14,869$ (1424–1691°K.; 0.0%)

CaF$_2$(1): $H_T - H_{298.16} = 23.88T - 930$ (1691–1800°K.; 0.0%)

Differentiating the above heat-content equations gives the specific heat relationships

MgF$_2$(s): $C_p = 16.93 + 0.00252T - (220,000/T^2)$
MgF$_2$(l): $C_p = 22.57$
CaF$_2$(α): $C_p = 14.30 + 0.00728T + (46,900/T^2)$
CaF$_2$(β): $C_p = 25.81 + 0.00250T$
CaF$_2$(1): $C_p = 23.88$

Discussion

No reliable values for the specific heats of either fluoride near room temperature appear in the literature. Heat content equations, based upon the first two experimental values obtained at temperatures immediately above 298.16°K. and zero heat content at 298.16°K., were derived for both substances and the specific heats at 298.16°K. obtained by calculation: MgF$_2$, $C_{p298.16} = 15.8$; and CaF$_2$, $C_{p298.16} = 17.0$. These derived values may be in error by a few per cent. but they are adequate for many purposes.

The specific heats of both liquid fluorides appear to be constant over the temperature ranges investigated. Measurements of liquid calcium fluoride covered slightly less than 100°, while those of liquid magnesium fluoride extended over about 220°; hence, a small curvature would be imperceptible.

To check the measurements on calcium fluoride in the temperature region 1,320 to 1,440°K., several determinations were made using a sample of reagent grade calcium fluoride. These agreed with the natural fluorite measurements well within the experimental error. Again no discernible discontinuity in the heat content curve was found in this temperature range.

Krestovnikov and Karetnikov[6,7] have made heat content measurements to 1,273°K. on both fluorides. Their results for magnesium fluoride in comparison with the present work are about 7% lower at 573°K., in good agreement at 973° and 1,073°K., and higher by 5% at 1,273°K. Their measurements of calcium fluoride are about 3% higher at 573°K., in fair agreement at 873° and 973°K., and lower by 4% at 1,273°K. They made no measurements in the liquid range of either substance.

Lyashenko[8] has reported measurements of calcium fluoride (not shown in Fig. 1) to 1,590°K. His results are consistently lower than the present work; the average deviation is about 3%.

Summary

High-temperature heat contents above 298.16°K. of magnesium fluoride and calcium fluoride (fluorite) were determined from room temperature to about 1,773°K. From these data heats of fusion and melting points also were obtained. The results have been summarized by algebraic equations and a table giving the heat content and entropy increments above 298.16°K. at 100° intervals.

(6) A. N. Krestovnikov and G. A. Karetnikov, *Legkie Metal.*, **8**, 29–31 (1934).

(7) A. N. Krestovnikov and G. A. Karetnikov, *ibid.*, **4**, 16–18 (1935).

(8) V. S. Lyashenko. *Metallurg.*, **10**, 85–98 (1935).

NOTES

Complexes of Neutral and Univalent Nickel

BY CLARA L. DEASY

By treating an anhydrous liquid ammonia solution of potassium cyanonickelate with excess potassium, Eastes and Burgess[1] obtained a compound of the formula K$_4$Ni(CN)$_4$. With the potassium cyanonickelate in excess, a different compound, K$_2$Ni(CN)$_3$, was obtained. It was found that the latter compound could also be prepared by treating an aqueous solution of potassium cyanonickelate with potassium amalgam.

No explanation of the state of valence of the nickel in these compounds was offered. On the basis of modern theory, however, electronic formulas for the compounds can be written in the usual way.

(1) Eastes and Burgess, THIS JOURNAL, **64**, 1187 (1942).

The negative radical of the compound K$_4$Ni(CN)$_4$, [Ni(CN)$_4$]$^{----}$, is isoelectronic with nickel carbonyl, which also contains neutral nickel. Accordingly an electronic configuration similar to that postulated for nickel carbonyl[2] is suggested. Three resonating structures can be considered:

(2) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 232.

B

C

Structure A seems more satisfactory than the single-bonded structures since the nickel atom is neutral, rather than negative; and in its general behavior nickel is electropositive rather than electronegative. It also has a stable octet of electrons about the carbon atom; this is not shown by structure C, which has only a sextet of electrons. In A four of the $3d$ orbitals of nickel, as well as the $4s$ orbital and one $4p$ orbital, would be used in bond formation.

Probably, as in the case of nickel carbonyl, the molecule resonates between the double-bonded and single-bonded structures. A more detailed discussion of the nature of the bonds and of their spatial configuration must await the determination of physical data.

It may be noted that chemically nickel carbonyl and the $[Ni(CN)_4]^{----}$ ion show a similarity in properties. Both, for example, are oxidized by air or oxygen and are decomposed by water.[1,3]

Two resonance structures are suggested for the $[Ni(CN)_3]^{--}$ ion:

D

E
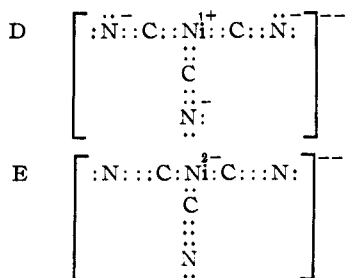
Formula D may make the greater contribution because here the nickel is electropositive. In this structure four $3d$ orbitals, the $4s$, and one $4p$ orbital might be used in bond formation, with the unpaired electron in a second $4p$ orbital. A similar structure can be postulated for E, with one $3d$, the $4s$, and one $4p$ orbital used for bond formation, and the lone electron in a $4p$ orbital.

Either of these would be an electronic configuration similar to that of cobalt in the $[Co(CN)_6]^{----}$ ion, in which it is postulated that

(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, p. 955.

the unpaired electron of cobalt occupies the outer unstable $4d$ orbital. This outer lone electron is believed to account for the instability of the complex[4]; this instability is evidenced, for example, by the liberation of hydrogen from water by the ion. The $[Ni(CN)_3]^{--}$ ion also decomposes water, liberating hydrogen; this chemical behavior gives support to the above formulation.

Again physical data are needed for complete elucidation of the structure.

(4) Pauling, ref. 2, p. 94.

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Isolation of Mannitol from the Seeds of Citrullus vulgaris[1,2]

BY W. MAYO HIGGINS[3] AND MELVIN F. W. DUNKER

In a phytochemical study of the seeds of Citrullus vulgaris Schrader, the common watermelon, d-mannitol was isolated from the alcohol extract of the defatted whole seeds. Separate extractions of the shells and kernels of the seeds showed mannitol to be present only in the shells. No previous reference to the isolation of d-mannitol from Citrullus vulgaris was found in the literature.

Experimental

Twenty pounds (9080 g.) of seeds was ground to pass a 20-mesh screen and exhaustively extracted in a Soxhlet type, stainless steel extractor successively with petroleum ether (b. p. 60–70°) and 95% alcohol.

The alcohol extract, 409 g. (4.3%) of a viscous reddish-brown material containing suspended solid, was washed by decantation successively with boiling ether, alcohol at room temperature, and warm alcohol (45°) until the washings were colorless in each case. Finally the solid residue was dissolved in boiling alcohol from which fine white needles crystallized on cooling. About 6 g. (0.065%) of crude material was obtained and purified by crystallization from 95% alcohol to a constant m. p. of 164.6–166.5° (cor.).

Elementary analysis and classification tests indicated a polyhydroxy alcohol or sugar. The m. p. corresponded to that recorded for d-mannitol and mixed m. p. with a known sample of d-mannitol gave no depression. The optical rotation was $[\alpha]^{26}D$ −0.86° (c, 1.6) in water and $[\alpha]^{22}D$ 27.75° (c, 3.03) in 7.4% aqueous solution of borax. The optical rotation of mannitol in water has been reported as levo,[4] $[\alpha]^{25}D$ −0.49°,[5] and $[\alpha]^{22}D$ −0.99,[6] and the rota-

(1) Abstracted from a part of the thesis of W. Mayo Higgins presented to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1943.

(2) The investigation of Citrullus vulgaris was begun under the direction of Dr. Lloyd M. Parks, now on leave of absence to the Armed Forces.

(3) Present address: Burroughs Wellcome and Co., Tuckahoe, New York.

(4) H. Landolt, "The Optical Rotating Power of Organic Substances," The Chemical Publishing Co., Easton, Pa., 1902, 2nd ed., p. 511.

(5) A. Grun, I. Husman and H. Nossowitsch, Monatsh., 37, 215 (1916).

(6) A. A. Dodge, Thesis, University of Wisconsin, 1941.