$(OH)^{-3}$ is predominant in the *p*H range 9 to 10. In strongly alkaline solutions, a mixture of mercury and mercuric oxide precipitates. Below about *p*H 6.5, insoluble mercurous pyrophosphate salts precipitate.

The Hg–Hg distance increases in the series Hg_2F_2, Hg_2Cl_2, Hg_2Br_2, Hg_2I_2; 2.43, 2.53, 2.58, 2.69 Å.[4] This plus the fact that complexing ligands such as NH_3 or CN^- cause disproportionation to Hg(II) and the metal suggest that the formation of a covalent bond between such a ligand and Hg_2^{++} diminishes the amount of *s* character in the Hg–Hg bond and thus weakens it. We then expect stable mercurous complexes only with strong "ionic" ligands, such as $P_2O_7^{-4}$, $C_2H_4(CO_2)_2^{--}$, etc., in accordance with our observations. Preliminary studies indicate that oxalate forms $Hg_2(C_2O_4)_2^{--}$ and $Hg_2(C_2O_4)(OH)^-$; this work is continuing.

---

[4] G. Grdenic, *J. Chem. Soc.*, 1312, 1316 (1956).

[5] This research has been supported by the AEC, Contract AT(11-1)-188; TY wishes to acknowledge gratefully the support of the Brazilian government via a CAPES fellowship.

CONTRIBUTION NO. 2468 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
TETSUO YAMANE[5]
NORMAN DAVIDSON

RECEIVED JUNE 1, 1959

PARTIAL MOLAL VOLUMES OF HYDROGEN AND DEUTERIUM

Sir:

In 1958 Jolley and Hildebrand published a paper[1] on Solubility, Entropy, and Partial Molal Volumes of Gases in Non-polar Solvents which included figures indicating that the partial molal volume of hydrogen is larger than that of deuterium in the same solvent. This is so interesting that we undertook the more careful determinations herein described.

The main improvement in technique, other than extreme care in all controls, has been to reduce the pressure in one of the two capillaries of the Horiuti dilatometer so as to keep the mercury in the other, open capillary always at the same level, thus avoiding an "apparent compressibility" correction for the increased head of mercury. There were no significant changes in barometric pressure during a run.

At least four additions of gas were made for each determination. In the absence of leaks or other errors, a plot of ΔV *vs.* moles of gas added gave points falling accurately on a straight line. Partial molal volumes, $\bar{v}$, were calculated from the slopes of these lines. These solutions were all so dilute that $\bar{v}$'s so determined are essentially the limiting values for infinite dilution.

Results are given in the table. The approximately 10% excess of $\bar{v}$ for hydrogen in benzene and toluene is very striking. We think the explanation lies in difference in zero-point energy. Although the temperature is far above 0°K., the potential "boxes" are very small. A quantitative treatment of the problem by John Walkley and Berni J. Alder is in preparation.

PARTIAL MOLAL VOLUMES OF HYDROGEN AND DEUTERIUM AT 25° AND 1 ATMOSPHERE

		Hydrogen	Deuterium
Benzene		35.1	32.7
		35.5	32.5
		35.4	32.7
	Av.	35.3	32.7
Toluene		35.7	32.3
		35.7	32.4
			32.4
	Av.	35.7	32.4
f-Heptane		54.5	52.9
		54.3	(53.4)
		54.3	52.9
	Av.	54.4	52.9

This work has been supported by the National Science Foundation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA
JOHN WALKLEY
JOEL H. HILDEBRAND

RECEIVED JULY 13, 1959

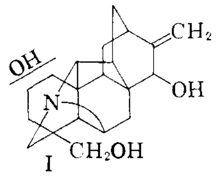
---

[1] J. E. Jolley and J. H. Hildebrand, THIS JOURNAL, **80**, 1050 (1958).

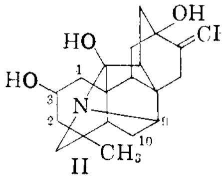
THE ACONITE ALKALOIDS. THE STRUCTURE OF HETISINE

Sir:

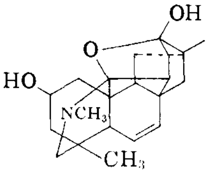
On the basis of Jacobs' data[1,2] and certain new considerations, Wiesner has proposed the hypognavine-like[3] structure I for hetisine.[4] In refutation of I and in support of structure II, we submit these data.



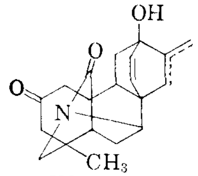
I



II



III



IV

The presence of an exocyclic methylene group in hetisine is shown by bands at 6.04 and 11.10 μ (KBr) which do not appear in the spectrum of dihydrohetisine, and is confirmed by the isolation of formaldehyde upon ozonolysis of hetisine. C-Methyl determinations (0.57 C-Me/mole)[5] and infrared studies indicate the existence of one C-methyl group in hetisine.

Jacobs' Hofmann data[2] appear to require rearrangement of an allylic alcohol.[4] The presence of a secondary allylic alcohol, as proposed by Wiesner[4] in I, is untenable. Such systems are oxidized easily

---

[1] W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **143**, 605 (1942).

[2] W. A. Jacobs and C. F. Huebner, *ibid.*, **170**, 189 (1947).

[3] S. Sakai, *Chem. and Pharm. Bull. (Japan)*, **6**, 448 (1958).

[4] K. Wiesner and Z. Valenta, *Fortsch. der Chemie*, **16**, 27 (1958).

[5] Atisine and isoatisine also average 0.5 C-Me/mole by this method.

to conjugated enones,[6] but hetisine, which has been oxidized to mono- and dicarbonyl compounds, gives no such enone. Further, the infrared spectrum of Jacobs' desmethylhetisine,[2] III, shows no $>C=O$ absorption but does have peaks at 8.75 and 8.99 μ consistent with a hemiketal formulation.[7] Similar peaks 8.72 and 8.98 μ, no $C=C$ absorption, are found in the spectrum of an aqueous sulfuric acid-catalyzed isomerization product of hetisine, m.p. 278–279.5°. (*Anal.* Found: C, 72.94; H, 8.04.)

CrO_3–pyridine oxidation of hetisine produces the keto-"lactam," IV, $C_{20}H_{23}NO_3$, m.p. 236–238° (*Anal.* Found: C, 74.01; H, 7.02). The low pK_a' of IV (6.72) compared to that of hetisine (9.85) (both in 1:1 methanol–water) is explicable in IV on the basis of inductive effect,[8] but is too great to be so explained by a carbonyl further removed from nitrogen than the α-position.[9,10] A comparison of the infrared spectrum of VI (5.82 μ with shoulder at 5.81 μ) with that of 2,2-dimethylquinuclidone-6 (5.77 μ)[11] is the basis of the assignment of an $N-C_9$ bond (bicyclo-2,2,2 system) rather than a $N-C_3$ or $N-C_{10}$ bond (bicyclo-2,2,1 system) to hetisine.[12] Base hydrolysis of IV produces a keto-carboxylate, 5.85 μ ($C=O$), 6.33 and 7.27 μ (CO_2^-).

Jacobs' oxidation product of dihydrodesmethylhetisine must be a carbinol–amine ether[3] because borohydride reduction reconverts it to dihydrodesmethylhetisine (infrared evidence) and because its spectrum shows reduced hydroxyl absorption, no carbonyl absorption, but has peaks at 8.67, 8.75, 8.90 and 9.07 μ (O—C—O and O—C—N). If the nitrogen is bonded to C_9 or C_{10}, the third hydroxyl must be *cis* to nitrogen and on C_3 or C_4. The stability of the hydrolysis product of IV leads us to tentatively assign the hydroxyl to C_3.[13]

THE ROCKEFELLER INSTITUTE[14]
NEW YORK 21, NEW YORK
A. J. SOLO
S. W. PELLETIER

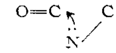
RECEIVED JUNE 17, 1959

---

[6] S. W. Pelletier and W. A. Jacobs, THIS JOURNAL, **76**, 4496 (1954).

[7] Models indicate that the ketone derived from the secondary alcohol in I would not be suitably disposed for internal hemiketal formation.

[8] 2,2-Dimethylquinuclidone-6 has a pKa' 5.33 (water)[11]; quinuclidine has a pKa' 10.65 (water).

[9] The low pKa's reported for some alkaloids having carbonyl groups γ or δ to the nitrogen atom undoubtedly are caused by transannular effects the type  C.[10] The stereochemistry of hetisine prohibits such an interaction.

[10] N. J. Leonard, R. C. Fox and M. Oki, *ibid.*, **76**, 5708 (1954).

[11] H. Pracejus, *Chem. Ber.*, 988 (1959).

[12] As no evidence has appeared to the contrary, hypognavine also may have a $N-C_9$ rather than an $N-C_{10}$ bond.

[13] If the hydroxyl is at C_4, then IV would give a β-ketocarboxylate on hydrolysis.

[14] This investigation was supported in part by grant RG5807 from the National Institutes of Health, United States Public Health Service.

BOOK REVIEWS

Gmelins Handbuch der Anorganischen Chemie. Achte Völlig Neu Bearbeitete Auflage Zirkonium. System-Nummer 42. E. H. ERICH PIETSCH, Editor. Verlag Chemie-G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1958. xxxvii + 448 pp. 17 × 25 cm. Price, Kart. DM 261.--; Geb. DM 266.--.

Gmelins Handbuch der Anorganischen Chemie. Achte Völlig Neu Bearbeitete Auflage. Hafnium. Ergänzungsband. System-Nummer 43. E. H. ERICH PIETSCH, Editor. Verlag Chemie, G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1958. ii + 23 pp. 17 × 25 cm. Price, Kart. DM 17.--; Geb. DM 22.--.

The high standards of the earlier volumes of the eighth edition of Gmelin have been continued in the digest of zirconium publications. Both the breadth of the coverage and the absence of errors in the details were noted with approval; the extensive use of diagrams and graphs is commendable. The discovery, geochemistry, and mineralogy of zirconium are covered in the first 50 pages. The treatment of ores and the applications of the metal and its compounds require 34 pages. Then a very complete discussion of the preparation of the element in various forms and of the physical properties is contained in the next 70 pages. The rest of the book describes the preparations and the properties of alloys and compounds of zirconium.

The short supplementary volume on hafnium devotes a proportionate amount of space to each of the above topics to review articles published mostly between 1940 and 1949. The Table of Contents shows in parallel columns the page numbers of the items in the supplement and in the main volume on hafnium, system number 43, published in 1941.

Although there are a few references to articles published after 1949 and some books published as late as 1957 are listed, the complete coverage as stated in the publication pages extends only through 1949 for both books. As examples of what can be done, the volume on selenium published in 1953 reviews the literature through 1952 and the volume on platinum published in 1957 reviews through 1953, and it seems unfortunate that the coverage for zirconium and hafnium, particularly the latter as a supplementary volume, was not extended beyond 1949.

Despite this limitation these books will be valuable additions to the shelves of every major chemistry library. One only wishes that a lower price could be established for individual purchasers, as is done by *Chemical Abstracts*, so that the specialist could afford pertinent volumes for his private library.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT
CARL W. MOELLER

Vapor-Liquid Equilibrium. By EDUARD HÁLA, JIŘÍ PICK, VOJTĚCH FRIED and OTAKAR VILIM. Translated by G. STANDART. Pergamon Press, Inc., 122 East 55th Street, New York 22, N. Y. 1958. xviii + 402 pp. 16 × 23.5 cm. Price, $14.00.

This book is intended primarily for the chemical engineer or technologist who is concerned with vapor-liquid composition data in the design and operation of fractional distillation equipment.

For convenience the book is divided into three parts. The first deals with the basic thermodynamic equations expressing the relation between the vapor-liquid composition and the temperature and pressure. An excellent review is given of the various methods that have been proposed for calculating these data. The practical value to the technologist is greatly enhanced by the inclusion of illustrative examples showing how to apply the theoretical equations.

In the second part the direct determination of vapor-liquid equilibrium data including the measurement of temperature and pressure and the correlation of the results, is described in considerable detail. Much helpful information is given about the design and operation, and the weak points