$(OH)^{-3}$ is predominant in the pH range 9 to 10. In strongly alkaline solutions, a mixture of mercury and mercuric oxide precipitates. Below about pH 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.

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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.

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

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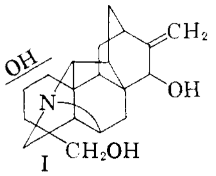
RECEIVED JULY 13, 1959

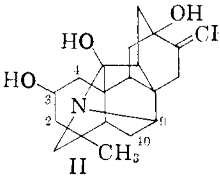
THE ACONITE ALKALOIDS. THE STRUCTURE OF HETISINE

Sir:

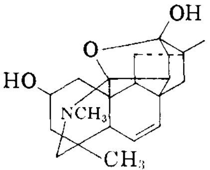
On the basis of Jacobs' data[1,2] and certain new considerations, Wiesner has proposed the hypognavine-like[3] structure I for hetisine.[4] In refutation of I and in support of structure II, we submit these data.



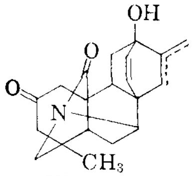
I



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.