

THE HEAT CAPACITY OF SOME HYDROGEN HALIDES AT HIGH TEMPERATURES AS CALCULATED FROM RAMAN SPECTRA

Sir:

The existing data on the heat capacity of the hydrogen halides in gaseous form are very meager and are on the whole unsatisfactory as Eastman [*Bur. Mines, Tech. Paper 445 (1929)*] has pointed out in his critical summary of the specific heats of gases. Experimental evidence on HBr, HI and HF is entirely lacking, while such data as are available for HCl leave something to be desired. Since the heat capacities of N₂ and HCl are practically identical in so far as one can tell from the fragmentary evidence on the latter, and since the energy of the lower levels in the molecules of HCl, HBr and HI is not very different from that of the corresponding level in N₂, Eastman assigned to the three halide gases the heat capacity of N₂, which is known with reasonable accuracy. This assumption, which admittedly introduces some error, was nevertheless the best one that could be made under the circumstances.

Since the methods heretofore employed in making heat capacity measurements at high temperatures have involved a difficult technique and have led in a great many cases to questionable results, it seems not unlikely that for a polar molecule calculations based on the well-known Planck-Einstein specific heat equation may in the end be more satisfactory than direct observations, in spite of the fact that such factors as the increases in potential energy due to stretching of the molecule are neglected.

Reliable values of the fundamental frequency of vibration of HCl, HBr and HI have recently been derived by Salant and Sandow [*Phys. Rev.*, **37**, 373 (1931)] from Raman spectra. Using their results (HCl, $\Delta^1/\lambda = 2886 \text{ cm.}^{-1}$, HBr, $\Delta^1/\lambda = 2558 \text{ cm.}^{-1}$, HI, $\Delta^1/\lambda = 2233 \text{ cm.}^{-1}$) it is possible to calculate the heat capacity of these gases with an accuracy apparently somewhat greater than that of the values selected by Eastman, which are probably the best of the existing data.

Such a calculation has been made and the results, expressed as C_p ($C_p = C_v + R$), are shown in the accompanying table. The single set of

TABLE I
HEAT CAPACITY OF HYDROGEN HALIDES

Temp., °K.	C_p HCl as calcd.	C_p HBr calcd.	C_p HI calcd.	C_p Eastman's best value
600	7.07	7.13	7.26	7.17
800	7.28	7.44	7.58	7.33
1000	7.54	7.71	7.86	7.50
1200	7.78	7.94	8.10	7.67
1400	7.98	8.12	8.28	7.86
1600	8.14	8.28	8.42	8.06
1800	8.28	8.40	8.53	8.27
2000	8.38	8.48	8.59	8.49

values chosen by Eastman as representing the heat capacity of all three halide gases has been included for comparison.

It will be seen that the agreement between Eastman's selected figures and the calculated values for HCl is satisfactory, the maximum deviation being approximately 1.5%. It is perhaps worth noting that above 2000° Eastman's values run higher than the calculated ones and that this is the same direction in which Eastman's values deviate from the best of the experimental observations.

For HBr and HI differences as great as 5% exist between the results of the calculations and the data of Eastman. Unfortunately there appear to be no experimental observations on which to check the calculations but in view of the agreement found with HCl it seems probable that the calculated values are not much in error and almost certainly give a closer description of the true heat capacity of these gases than is obtained by assigning the same figure to all.

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THE CHLORINATION OF NEOPENTANE

Sir:

All recorded methods of making neopentane failed to give appreciable yields except that of Lwow [*Z. Chem.*, 520 (1870)] involving dimethyl zinc and a tertiary butyl halide. The iodide, bromide and chloride gave 42, 46 and 51% yields, respectively. The hydrocarbon froze and boiled at approximately -20 and $+10^{\circ}$, respectively.

The chlorination of neopentane was very easy. At room temperature in diffused light the color of chlorine disappeared in fifteen minutes. The chloride boiled at 24° (80 mm.) and froze at -20° . The analysis for chlorine was 1.5% low for an amyl chloride. Tertiary amyl chloride showed b. p. 23.5° (8 mm.) and m. p. -73° . A small amount of a dihalide, b. p. 35° (8 mm.), was also obtained. The monochloride when shaken with cold water for thirty minutes showed the presence of 6% of tertiary halide (Michael). The amount of tertiary halide was increased only slightly, if at all, by heating the chloride at 140° for one and one-half hours. All known methods of converting a halide to a Grignard reagent failed. These facts indicate that the halide obtained is neopentyl chloride.

Neopentane is being prepared in larger amounts to make possible a more thorough study of its chlorination in relation to the mechanism of rearrangements. The limited amount of tertiary amyl chloride formed and the surprising stability of the neopentyl chloride carry implications of great