THERMODYNAMIC FUNCTIONS OF FORMALDEHYDE*

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Thermodynamic properties of ideal gaseous formaldehyde have been calculated from recent accurate infra-red and microwave spectroscopic data. The results obtained differ considerably from the latest published thermodynamic data.

The thermodynamic functions of formaldehyde have been previously calculated by Stevenson and Beach (1938) and by Thompson (1941). The calculations of Stevenson and Beach are based on old physical constants and on inaccurate molecular data so that the resultant functions are considerably different from the true functions. Thompson has used more recent molecular data but his results are somewhat inconsistent, particularly at high temperatures.

Recently accurately determined fundamental frequencies and moments of inertia of the formaldehyde molecule make it worthwhile to recalculate the thermodynamic functions of formaldehyde.

Calculations

The fundamental frequencies used are given by Herzberg (1945) and these are 1167, 1280, 1503, 1744, 2780, and 2874 cm^{-1}. The moments of inertia have been determined from accurate microwave spectra of formaldehyde (Lawrence and Strandberg 1951 ; Erlandsson 1956). The three moments are $2 \cdot 974$, $21 \cdot 603$, and $24 \cdot 668 \times 10^{-40}$ g cm^2.

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Assuming harmonic vibrations, no rotational distortion, and no rotation-vibration coupling the standard equations of statistical mechanics can be used. When the necessary data become available to correct for above assumptions the corrections can be expressed in the form of $1/T$, $\log T$, and power series of T, and added to the calculated functions (Kassel 1936).

For consistency with existing thermodynamic functions of compounds the fundamental constants from Rossini *et al.* (1952) have been used, and the principal constant R was taken as 1·98719 cal/deg mole. The resultant equation for the translational and rotational contributions to the free energy function was

$$\left(\frac{F^0-H_0^0}{T}\right)_{tr}+\left(\frac{F^0-H_0^0}{T}\right)_{rot}=-257\cdot381-4R\log T-\frac{3}{2}R\log M$$
$$-\tfrac{1}{2}R\log(I_1I_2I_3)+R\log s,$$

where F^0 is the free energy of the ideal gaseous molecule, H_0^0 is the value of the free energy at 0 °K, T is the absolute temperature, M the molecular weight, I_1, I_2, and I_3 the principal moments of inertia, and s the symmetry number. The related equations can be found in standard textbooks (Herzberg 1945) or reviews (Wilson 1940). The calculations have been carried out from first principles using a calculating machine, and these have been checked using tables of Einstein functions (Sherman and Ewell 1942).

TABLE 1

THERMODYNAMIC FUNCTIONS OF FORMALDEHYDE IN IDEAL GASEOUS STATE

T (°K)	$H^0-H_0^0$ (cal/mole)	$(H_0^0-F^0)/T$ (cal/mole °K)	S^0 (cal/mole °K)	C_p^0 (cal/mole °K)
298·16	2393·8	44·227	52·256	8·441
300	2410·0	44·277	52·309	8·458
400	3296·9	46·613	54·855	9·349
500	4284·9	48·485	57·055	10·418
600	5380·2	50·082	59·049	11·479
700	6578·0	51·497	60·894	12·459
800	7868·5	52·780	62·616	13·336
900	9241·5	53·964	64·232	14·106
1000	10686·4	55·067	65·753	14·776
1100	12193·6	56·105	67·190	15·355
1200	13754·8	57·086	68·548	15·855

Results

The calculated results are given in Table 1. The results are given to five significant figures although the accuracy does not in general warrant more than four figures. The extra figure will be useful for interpolation and calculation of differences, and will allow the addition of anharmonicity and other correction terms without recalculation of the functions.

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