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Note on the Heat Capacities and Energies of $SiCl_4$, $TiCl_4$ and $SnCl_4$

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THE interest in thermodynamic functions calculated from spectroscopic data is the reason for tabulating some information that has been available to us for some time. The heat capacities and energies of $SiCl_4$, $TiCl_4$ and $SnCl_4$ were calculated by means of well-known formulae.[1] The frequencies (liquid) employed were taken from Kohlrausch[2] and are given in Table I along with their degeneracies in parentheses. Since the molecules investigated are nonpolar there should be no great difference in the calculated functions if we employ the frequencies obtained from the liquids rather than the gases. In fact, for gaseous $SnCl_4$ the frequencies ν_1 and ν_3 are 367 and 400 cm^{-1} [3] as compared to 367 and 401 cm^{-1} for the liquid. The heat capacity in cal./mole deg. for each gas in its standard state is tabulated in Table II and in Table III we have tabulated the energies in cal./mole. Since these molecules have low frequencies and anharmonicity corrections are not available, the calculation was not carried beyond 300°C. Table IV gives the only experimental heat capacity data[4] that could be found for these tetrachlorides in the gaseous phase and as can be seen the calculated values agree fairly well. The ice point on the Kelvin scale has been taken as 273.1°K and the fundamental constants employed were those given by Birge.[5]

TABLE I.

	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
$SiCl_4$	422 cm^{-1}	148 cm^{-1}	608 cm^{-1}	220 cm^{-1}
$TiCl_4$	386	119	491	139
$SnCl_4$	367	104	401	136

TABLE II. *Heat capacities in cal./mole deg.*

T°C	$SiCl_4$		$TiCl_4$		$SnCl_4$	
	C_{vib}	C_p	C_{vib}	C_p	C_{vib}	C_p
0	13.19	21.14	14.50	22.45	15.24	23.19
10	13.41	21.36	14.68	22.63	15.39	23.34
20	13.63	21.58	14.85	22.80	15.53	23.84
30	13.83	21.78	15.01	22.96	15.66	23.61
40	14.02	21.97	15.16	23.11	15.78	23.73
50	14.20	22.15	15.29	23.24	15.90	23.85
60	14.37	22.32	15.42	23.37	16.00	23.95
70	14.52	22.47	15.54	23.49	16.09	24.04
80	14.68	22.63	15.65	23.60	16.19	24.14
90	14.81	22.76	15.75	23.70	16.26	24.21
100	14.94	22.89	15.85	23.80	16.34	24.29
200	15.92	23.87	16.55	24.50	16.89	24.84
300	16.48	24.43	16.94	24.89	17.19	25.14

TABLE III. $E^0-E_0^0$ *cal./mole.*

T°C	$SiCl_4$	$TiCl_4$	$SnCl_4$
0	3576	4031	4217
20	3962	4444	4645
50	4557	5075	5294
100	5583	6152	6400
200	7726	8377	8664
300	9936	10650	10970

TABLE IV.

	T°C	C_p cal./mole deg.
$SiCl_4$	90–234	22.5
$TiCl_4$	136–271	24.5
$SnCl_4$	149–273	24.5

[1] For instance, see Fowler, *Statistical Mechanics* (Macmillan, 1936).
[2] Kohlrausch, *Der Smekal-Raman-Effekt* (Berlin, 1931).
[3] Braune and Engelbrecht, Zeits. f. physik. Chemie **B19**, 303 (1932).
[4] Regnault, Mém. de l'Acad. **26**, 1 (1862).
[5] Birge, Phys. Rev. Sup. **1**, 1 (1929).