Thermodynamic Function of Carbonyl Chloride

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work and Argonne National Laboratory, particularly Miss Gladys Swope, for irradiation and dosimetry services.

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Determination of the Speed of Sound in Sulfurhexafluoride in a Shock Tube*

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THE method of measuring sound speed from the head of a rarefaction wave in a shock tube[1] was applied to SF_6. It was found that at 30.0°C and 750 mm Hg the sound speed had a value of 454.5 ± 0.5 ft/sec. The probable error of the mean was based on 11 runs. This result agrees quite closely with 451 ft/sec calculated from the acoustic relation $a^2=\gamma RT$. The value of γ was calculated for SF_6 in equilibrium with translation, rotation, and vibration excited.[2] Using the vibrational frequencies of SF_6, at a temperature of 30.0°C, it was found that $\gamma=1.093$. This value is in good agreement with that calculated from an empirical relation.[3] Commercial SF_6 was used for the experiments.[3] It contained traces of water and other impurities.

The above result for the sound speed was also obtained by using weak shock waves. The shocks were weak enough that they gave acoustic reflection at the closed end of the shock-tube channel.

It might be noted that when a Beattie-Bridgeman equation of state is used to calculate the speed of sound, a lower result of 447 ft/sec is obtained, as expected.

Interferograms of the transition through the rarefaction wave and shock wave were also taken. The rarefaction wave profiles were regular at the head of the wave. There was no indication of additional wave heads that might travel at a sound speed corresponding to a $\gamma=5/3$ or $\gamma=4/3$. These are the so-called "frozen" sound speeds, with vibration and rotation not participating or the vibrational modes not excited, respectively. The transition through the weak shocks exhibited a compression wave profile at the center of the steam. The shock waves near the center of the tube were curved and then became normal to the wall. The profile near the wall appeared to steepen to an apparent discontinuous shock. A diffuse shock wave zone was not distinguishable.[4] However, this is not unexpected owing to the short vibrational relaxation time for SF_6 ($\sim 6\times 10^{-7}$ sec).[2,5]

The rarefaction wave and the formation of the shock wave could also be observed at the origin using (x,t)-plane schlieren records. However, curvature of the head of the rarefaction wave[6] could not be detected at a film speed of 220 ft/sec. Again, owing to the very short relaxation time of SF_6, it would perhaps only be possible to observe such effects extremely close to the origin of an ideal centered wave with a very high-speed streak camera, since the time of observation of these effects would be of the order of the vibrational relaxation time.[7,8] However, owing to the breaking process at the diaphragm, the rarefaction wave is not centered at the origin,[9] and an ideal centered rarefaction wave generated from wave interactions would be more useful for this purpose.

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Thermodynamic Function of Carbonyl Chloride

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CARBONYL chloride is an important reagent in organic synthesis, and may be a significant constituent of flames in the region 1000–3000°K when carbon, oxygen, and chlorine are present. Thompson[1] gives thermodynamic data up to 1000°K only. His table was accordingly extended to 4000°K, using harmonic-oscillator tables[2] and neglecting rotational stretching, rotation-vibration interactions, and anharmonicity. The six fundamentals given by Thompson are 230, 302, 444, 570, 845, and 1827 cm^{-1}. Equilibrium constants of dissociation into CO and 2Cl were computed, using free-energy data compiled by Gordon[3] and a standard heat of formation of -53.30 kcal/mole as given by the National Bureau of Standards.[4] Thompson's rotational and translational contributions to entropy and free-energy function were not checked. Data were calculated at 900°, 1100°, and every 200° between 1200° and 4000°,

TABLE I. Thermodynamic functions of Cl_2CO.

T	$\frac{-(F^0-E_0^0)}{T}$	$\frac{(H^0-E_0^0)}{T}$	S^0	C_p^0	H_{298}^T kcal/mole	log$K$	K
°K	←cal/mole °K			→			Atmos²
298.16	58.16	11.01	69.17	14.51	0	−49.778	1.667×10^{-50}
300	58.22	11.04	69.26	14.53	0.027	−49.394	4.037×10^{-50}
400	61.53	12.08	73.61	15.77	1.545	−33.909	1.233×10^{-34}
500	64.35	12.90	77.25	16.61	3.164	−24.604	2.489×10^{-25}
600	66.75	13.57	80.32	17.23	4.853	−18.382	4.150×10^{-19}
700	68.87	14.30	83.10	17.71	6.605	−13.932	1.170×10^{-14}
800	70.82	14.58	85.40	18.07	8.40	−10.601	2.506×10^{-11}
900	72.53	15.05	87.52	18.38	10.26	−7.997	1.007×10^{-8}
1000	74.14	15.35	89.49	18.59	12.08	−5.922	1.197×10^{-6}
1100	75.62	15.65	91.27	18.77	13.95	−4.222	5.998×10^{-5}
1200	76.99	15.91	92.90	18.92	15.82	−2.805	1.567×10^{-3}
1300	78.24	16.14	94.37	19.03	17.30	−1.599	2.518×10^{-2}
1400	79.48	16.36	95.84	19.14	19.64	−0.581	2.625×10^{-1}
1500	80.59	16.54	97.13	19.22	21.56	+0.314	2.061
1600	81.70	16.72	98.42	19.30	23.48	1.084	1.213×10^{1}
1700	82.70	16.87	99.56	19.36	25.42	1.774	5.943×10^{1}
1800	83.69	17.01	100.70	19.41	27.35	2.378	2.388×10^{2}
1900	84.58	17.14	101.72	19.45	29.30	2.930	8.512×10^{2}
2000	85.47	17.26	102.73	19.49	31.25	3.419	2.624×10^{3}
2100	86.31	17.36	103.67	19.52	33.20	3.863	7.295×10^{3}
2200	87.14	17.46	104.60	19.55	35.14	4.261	1.824×10^{4}
2300	87.91	17.55	105.46	19.58	37.11	4.630	4.266×10^{4}
2400	88.68	17.64	106.32	19.60	39.07	4.961	9.14×10^{4}
2500	89.39	17.72	107.10	19.62	41.03	5.273	1.88×10^{5}
2600	90.09	17.79	107.88	19.64	42.99	5.557	3.61×10^{5}
2700	90.76	17.86	108.62	19.66	44.97	5.821	6.63×10^{5}
2800	91.43	17.93	109.36	19.67	46.94	6.062	1.15×10^{6}
2900	92.04	17.99	110.03	19.69	48.90	6.293	1.964×10^{6}
3000	92.66	18.04	110.70	19.70	50.85	6.504	3.192×10^{6}
3100	93.24	18.10	111.34	19.71	52.83	6.704	5.058×10^{6}
3200	93.83	18.15	111.98	19.72	54.81	6.888	7.727×10^{6}
3300	94.39	18.20	112.59	19.73	56.78	7.061	1.151×10^{7}
3400	94.96	18.24	113.20	19.74	58.75	7.220	1.660×10^{7}
3500	95.45	18.28	113.73	19.74	60.71	7.382	2.410×10^{7}
3600	95.95	18.32	114.27	19.75	62.68	7.533	3.412×10^{7}
3700	96.44	18.36	114.80	19.75	64.66	7.672	4.699×10^{7}
3800	96.94	18.40	115.34	19.76	66.65	7.801	6.324×10^{7}
3900	97.39	18.43	115.82	19.76	68.61	7.930	8.512×10^{7}
4000	97.85	18.46	116.31	19.77	70.57	8.050	11.22×10^{7}

Note: $K_{COCl_2}=\frac{P_{CO}P_{Cl}^2}{P_{COCl_2}}$ $Cl_2CO\rightarrow CO+2Cl+83.106$ kcal at 0°K

84.908 kcal at 298.16°K.

and interpolated at intermediate temperatures. Equilibrium constants were calculated at every 100°. The data are summarized in Table I. Interestingly, the equilibrium constant of dissociation is about 1 at 1500°K compared to 2700°K for carbonyl fluoride.[3] Presumably carbonyl bromide is even less stable.

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Shock Tube Study of Dissociation Relaxation in Oxygen*

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THE shock tube studies of dissociation relaxation in oxygen reported here were motivated by recent experimental work at this Laboratory on the kinetics of the formation of nitric oxide from oxygen and nitrogen in the 2000° to 3000°K temperature range.[1] Analysis of these experiments indicates that this reaction follows