

The Thermodynamic Functions of the Chloro and Bromomethanes, Formaldehyde and Phosgene

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The Thermodynamic Functions of the Chloro- and Bromomethanes, Formaldehyde and Phosgene

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By use of the harmonic oscillator-rigid rotator approximation the free energy function $(F^0 - E_0^0/T)$, and the heat content $(H^0 - E_0^0)$ of the chloro- and bromomethanes, formaldehyde and phosgene have been calculated from spectroscopic and electron diffraction data over temperature ranges where the aforesaid approximations are valid. The heat capacity C_p for the bromomethanes, formaldehyde and phosgene have been calculated over the same temperature range as the free energy function and the heat content. The entropies of the ten molecules in the hypothetical ideal gas state at 298.1°K have been calculated. With the values of $(F^0 - E_0^0/T)$ for β -graphite, chlorine, oxygen and hydrogen tabulated by other investigators with our values of this function for the chloromethanes, formaldehyde and phosgene and the heat data of Bichowsky and Rossini we have calculated the free energy of formation of these molecules.

THE great interest in Raman and infrared spectroscopy in recent years has made available data on the fundamental vibration frequencies of a large number of molecules. This is particularly true of organic molecules. There is little prospect of immediate knowledge of the anharmonicity and vibration-rotation interaction constants becoming available for most polyatomic molecules. These data taken with the moments of inertia calculable from electron diffraction data on structures is sufficient to calculate the thermodynamic functions of the molecules in the hypothetical ideal gas state to the rigid rotator, harmonic oscillator approximation. The accuracy of calculations to that approximation has been discussed by Mayer, Brunauer and Mayer^{1a} and Gordon.^{1b, c} Among the halogen methanes only the energy content and heat capacity have been calculated by Vold² for the chloromethanes and the entropy of carbon tetrachloride at two temperatures by Lord and Blanchard.³ It seemed worth while to us to extend the work of Vold to the calculation of the entropy and free energy function of the chloromethanes as well as calculating the heat content, entropy, free energy and heat capacity of the bromomethanes, formaldehyde and phosgene.

The theory and methods of calculating thermodynamic functions from spectral data have been amply summarized by Kassel.⁴ This excellent review makes it unnecessary to discuss the methods used further than saying we have used Kassel's Eqs. (65) for calculating the vibrational contributions. For the rotational contributions we have used formulae derivable⁵ from Kassel's (49) or (50). When a knowledge of the stretching and anharmonicity constants becomes available the logarithm of the sum, $\sum_i f_i g_i$, (Eq. (63), reference 4) may be added with the proper multiplier to our functions to obtain more accurate values of the quantities in question.

When there are isotopic species of the molecules for which one is calculating the thermodynamic functions it is customary to evaluate the functions for each isotopic species and take a weighted mean as the value of the function for the naturally occurring mixture.^{6, 3, 4} For diatomic molecules of the type $A_2^{m_1}$, $A^{m_1}A^{m_2}$ and $A_2^{m_2}$ one can show that only a small error is made by taking chemical atomic weights and average frequencies in calculating the values of the partition functions. If the relative abundance of A^{m_1} is " a ," then the average molecular weight is $(am_1 + (1-a)m_2)$, the average moment of inertia is $1/2(am_1 + (1-a)m_2)e^2$, (d the nuclear

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¹ (a) Mayer, Brunauer and Mayer, *J. Am. Chem. Soc.* **55**, 50 (1933); (b) Gordon and Barnes, *J. Chem. Phys.* **1**, 692 (1933); (c) Gordon, *ibid.* **2**, 65 (1934).

² Vold, *J. Am. Chem. Soc.* **57**, 1192 (1935).

³ Lord and Blanchard, *J. Chem. Phys.* **4**, 707 (1936).

⁴ Kassel, *Chem. Rev.* **18**, 277 (1936).

⁵ Fowler, *Statistical Mechanics*, Chapters 5 and 6 (Cambridge Press, 1936).

⁶ Giauque and Overstreet, *J. Am. Chem. Soc.* **54**, 1731 (1932).

TABLE I. *The entropy of CCl₄ at 298.1°K.*

Lord and Blanchard ³	74.05 E.U.
This research.....	74.17 E.U.

separation), and the average frequency is $(1/2\pi)(2k/(am_3 + (1-a)m_2))^{1/2}$ where k is the force constant. Substitution of these values in the partition functions, $f_{\text{trans}}(T) = (2\pi mkT/h^2)^{3/2} V$, $f_{\text{rot}}(T) = 8\pi^2 I kT/h^2$ and $f_{\text{vib}}(T) = kT/h\nu$,⁷ and comparing with the weighted averages shows that the error made is less than $((m_2 - m_1)/m_1)^2$ in each partition function. For chlorine with isotopes 35 and 37 this would be an error of less than 0.4 percent in each partition function or less than 0.03 E.U. in the entropy. We have used this simplification throughout our calculations on molecules containing chlorine and bromine. A comparison of our value for the entropy of carbon tetrachloride at 298.1°K with that of Lord and Blanchard indicates the accuracy of carrying this approximation over to polyatomic molecules. (See Table I.)

The use of the symmetry number has been discussed in several papers.^{1, 3, 6, 8} Following Giauque and Overstreet⁶ we have ignored the existence of isotopic molecules in choosing the symmetry number for the various molecules considered. The symmetry numbers used are given in Table II.

THE HALOGEN METHANES

The frequencies given by Sponer⁹ for the chloro- and bromomethanes were used in cal-

⁷ The classical limiting form of the vibrational partition function is assumed here for simplicity.

⁸ Gordon and Barnes, *J. Phys. Chem.* **36**, 2601 (1932).

⁹ Sponer, *Molekulspektren*, Vol. I, Table 14 (Springer, 1935).

TABLE III.

C-Cl = 1.76Å	C-Br = 1.91Å	C-H = 1.09Å
∠H-C-H = 111°	∠Cl-C-Cl = 112°	CH ₂ Cl ₂ and CHCl ₃
In methylene bromide	∠Br-C-Br = 111°	
In bromoform	∠Br-C-Br = 112°	

culating the vibrational contribution to the various thermodynamic functions. The frequency $\delta'_t ||$ is not given by Sponer. Kohlrausch¹¹ gives 1054 cm⁻¹ for this frequency. In the case of methylene bromide two frequencies are missing in Sponer's tabulation. From the more recent work of Gockel,¹⁰ Kohlrausch¹¹ and Trumpy¹² we have taken the vibrations $\delta'_t ||$ and $\delta^2 \perp$ to be 806 and 487 cm⁻¹, respectively.

The internuclear distances and bond angles were taken for the chloromethanes from the review paper of Brockway.¹³ These constants for the bromomethanes were taken from the recent publication of Levy and Brockway.¹⁴ A slight distortion of the hydrogen-carbon-hydrogen angle from the tetrahedral angle in the direction to be expected from electrostatic repulsion was assumed for the methyl and methylene chlorides and bromides. This assumption is practically without effect on the moments of inertia so calculated. Table III gives the values we have used.

The calculations for molecules with several low frequencies were not carried to as high temperatures as were those for the molecules all of whose frequencies were reasonably large. The lack of the anharmonicity corrections would make high temperature calculations for the

¹⁰ Gockel, *Zeits. f. physik. Chemie* **B29**, 87 (1935).

¹¹ Kohlrausch, *ibid.* **B29**, 288 (1935).

¹² Trumpy, *Zeits. f. Physik* **100**, 250 (1936).

¹³ Brockway, *Rev. Mod. Phys.* **8**, 231 (1936).

¹⁴ Levy and Brockway, *J. Am. Chem. Soc.* **59**, 1662 (1937).

TABLE II. *The frequencies of the chloro- and bromomethanes used.*

	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CH ₃ Br	CH ₂ Br ₂	CHBr ₃	CBr ₄
$\nu_1 $	732 cm ⁻¹	2985 cm ⁻¹	3018 cm ⁻¹	459 cm ⁻¹	610 cm ⁻¹	2988 cm ⁻¹	3021 cm ⁻¹	265
$\nu_1^2 $	2900	700	667	775 ³	2900	576	539	667 ³
$\nu' \perp$	3047 ²	3049	760 ²		3061 ²	3060	654 ²	
$\nu^2 \perp$		738				636		
$\delta_1^1 $	1355	1054	366	313 ³	1305	(806)	222	183 ³
$\delta_1^2 $		284				174		
$\delta^1 \perp$	1020 ²	1153	1216 ²		957 ²	1090	1144 ²	
$\delta^2 \perp$	1460 ²	899	260 ²	217 ²	1450 ²	(478)	154 ²	123 ²
δ		1417				1390		
σ	3	2	3	12	3	2	3	12

The superscripts on the frequencies are the degeneracies of the vibrations.

molecules with several low frequencies quite uncertain.

FORMALDEHYDE AND PHOSGENE

Table IV gives the frequency assignments used for formaldehyde and phosgene. The formaldehyde values are from Sponer.⁹ The frequency, ν_t' , using the designation of Sponer, has been displaced upward by an interaction with $2\delta_t$, and should be somewhat lower than 2970. If the identification of Sponer for ν_t and $2\delta_t$ are reversed, ν_t' has been displaced downward and should be higher than 2780. We have used the round figure 2900 cm^{-1} since even at 1500°K this frequency contributes only 0.065 cal. per °K per mole to the free energy function. The Raman frequencies used for phosgene are those given by Ananthakrishnan.¹⁵ The agreement between his data and those of Dadiou and Kohlrausch¹⁶ is very good. Only five frequencies have been observed for phosgene. The calculations were made using only those five frequencies. The missing frequency ($\delta \perp^1$ or $\delta \perp^2$) would probably be not less than 300 cm^{-1} if the difference between these two frequencies in formaldehyde and in methylene chloride can be used as a guide. The values of $(F^0 - E_0^0/T)$ would be high by 0.25*R* cal. per mole per °K at 298°K and high by 0.64*R* at 600°K if this frequency were 300 cm^{-1} . This would amount to an error of 1 percent at 298°K and 2 percent at 600°K. When a value for this frequency is determined the necessary corrections in our tabulated values can be easily made by use of the tables of Gordon and Barnes.¹⁷

A third law calculation of the entropy of phosgene taken with our calculation of its entropy with one frequency missing could be used to fix

TABLE IV.

	FORMALDEHYDE	PHOSGENE
ν_t'	2900 cm^{-1}	573
$\nu \perp$	2800	832
ν_t''	1744	1807
δ_t	1461	302
$\delta \perp^1$	1039	442
$\delta \perp^2$	917	

¹⁵ Ananthakrishnan, Proc. Ind. Acad. Sci. **VA**, 285 (1937).

¹⁶ Dadiou and Kohlrausch, Mon. f. Chemie **57**, 225 (1931).

¹⁷ Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).

TABLE V.

H ₂ CO	$I_A = 24.33 \times 10^{-40}$	$I_B = 21.4 \times 10^{-40}$	$I_C = 2.9 \times 10^{-40}$
Cl ₂ CO	C-Cl = 1.68Å	C-O = 1.28Å	$\angle \text{Cl-C-Cl} = 117^\circ$

the magnitude of the unknown frequency. The heat capacities tabulated in Table IX together with equation of state data and measured gaseous heat capacities offer an alternative method for fixing this frequency. The various measurements of the equilibrium constant for the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$,¹⁸ are not sufficiently accurate to determine ΔS to better than about 2 E.U. hence the possibility of determining S_{COCl_2} from equilibrium measurements at the present time is ruled out.

The moments of inertia for formaldehyde were also taken from Sponer.⁹ Those of phosgene were calculated from the bond distance and bond angle values of Brockway, Beach and Pauling.¹⁹ Table V gives these constants for formaldehyde and phosgene.

The free energy function and the heat content of formaldehyde and phosgene are given in Table VI. The units and standard state are the usual ones.

In Table VII we have tabulated the entropies of the gases in the hypothetical ideal gas state at 298.1°K.

TABLE VI.

	H ₂ CO		Cl ₂ CO	
	$\frac{F^0 - E_0^0}{T}$	$(H^0 - E_0^0)$	$\frac{F^0 - E_0^0}{T}$	$(H^0 - E_0^0)$
291.1	45.872	2.364	59.065	2.870
298.1	46.265	2.432	59.299	2.966
350	47.580	2.902	60.930	3.637
400	48.701	3.388	62.343	4.321
500	50.632	4.440	64.835	5.754
600	52.291	5.596	66.984	7.256
700	53.764	6.848	68.886	8.812
800	55.097	8.186	70.595	10.409
900	56.329	9.599	72.150	12.036
1000	57.473	11.078		
1100	58.550	12.616		
1200	59.563	14.202		
1300	60.521	15.830		
1400	61.437	17.498		
1500	62.309	19.198		

¹⁸ (a) Bodenstein and Dunant, Zeits. f. physik. Chemie **61**, 437 (1908); (b) Bodenstein and Plaut, ibid. **110**, 399 (1924); (c) Atkinson, Heycock and Pope, J. Chem. Soc. **117**, 1410 (1920).

¹⁹ Brockway, Beach and Pauling, J. Am. Chem. Soc. **57**, 2693 (1935).

TABLE VII.

Substance	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CH ₃ Br
S° 298.1	55.99	64.68	70.82	74.17	58.74
Substance	CH ₂ Br ₂	CHBr ₃	CBr ₄	H ₂ CO	Cl ₂ CO
S° 298.1	70.84	79.14	85.59	52.42	67.24

THE FREE ENERGY OF FORMALDEHYDE

Bichowsky and Rossini²⁰ from the data of von Wartenberg, Muchlinski and Riedler²¹ estimate for the reaction $C_{\beta g} + H_2 + \frac{1}{2}O_2 = H_2CO$, $\Delta H_{291}^0 = -28.48$ Kcal./mole. $(H^0 - E_0^0)_{291}$ is 0.239 Kcal. for β -graphite,²² 2.022 Kcal. for oxygen, 1.975 Kcal. for hydrogen and 2.364 Kcal. for formaldehyde. Adding one gets $\Delta E_0^0 = -27.62$ Kcal./mole.

Newton and Dodge²³ have measured directly the equilibrium constants for $H_2 + CO = H_2CO$,

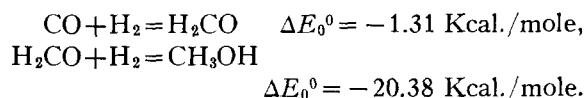
²⁰ Bichowsky and Rossini, *Thermochemistry* (Rheinhold, 1936), p. 45.

²¹ Zeits. f. angew. Chemie 37, 457 (1924).

²² Landolt-Börnstein, *Tabellen*.

²³ Newton and Dodge, J. Am. Chem. Soc. 55, 4758 (1933).

(1) and $H_2 + H_2CO = CH_3OH$, (2). They give as the best values, $K_1 = 1.72 \times 10^{-5}$ (520°K) and $K_2 = 2.09 \times 10^{-3}$ (470°K). Using Giauque's²⁴ value for $(F^0 - E_0^0)/T$ for hydrogen, Clayton and Giauque's²⁵ value for CO, and Kassel's²⁶ value for CH_3OH , it is possible to calculate $\Delta(F^0 - E_0^0)/T$ for each of these reactions at the temperature at which the equilibrium constants have been determined. Doing so we find for $CO + H_2 = H_2CO$, $\Delta(F^0 - E_0^0)/T_{520} = 24.30$, and for $H_2 + H_2CO = CH_3OH$, $\Delta(F^0 - E_0^0)/T_{470} = 29.16$. Since $\Delta F^0 = -RT \ln K$ and $\Delta E_0^0 = \Delta F^0 - T\Delta(F^0 - E_0^0)/T$ we have,



Now $C_{\beta g} + \frac{1}{2}O_2 = CO$, $\Delta E_0^0 = -27.40$,²⁵ and $C_{\beta g}$

²⁴ Giauque, J. Am. Chem. Soc. 52, 4826 (1930).

²⁵ Clayton and Giauque, J. Am. Chem. Soc. 54, 2610 (1932).

²⁶ Kassel, J. Chem. Phys. 4, 493 (1936).

TABLE VIII.

T°K	CH ₃ Cl		CH ₂ Cl ₂		CHCl ₃		CCl ₄	
	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$(H^0 - E_0^0)$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$(H^0 - E_0^0)$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$H^0 - E_0^0$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$H^0 - E_0^0$
291.1	49.43	2.422	56.58	2.765	61.14	3.287	61.95	3.996
298.1	49.63	2.496	57.10	2.859	61.41	3.405	62.28	4.145
350	50.99	3.018	58.68	3.527	63.30	4.244	64.59	5.203
400	52.16	3.573	60.06	4.232	64.96	5.113	66.63	6.282
500	54.22	4.812	62.52	5.781	67.94	6.978	70.29	8.542
600	56.04	6.207	64.71	7.479	70.58	8.972	73.50	10.892
700	57.69	7.741	66.70	9.300	72.95	11.060		
800	59.21	9.343	68.51	11.214	75.10	13.220		
900	60.63	11.158						
1000	61.97	12.998						
1100	63.23	14.926						
1200	64.44	16.923						

	CH ₃ Br		CH ₂ Br ₂		CHBr ₃		CBr ₄	
	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$H^0 - E_0^0$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$H^0 - E_0^0$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$H^0 - E_0^0$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$H^0 - E_0^0$
291.1	52.01	2.467	61.94	3.071	68.01	3.701	70.81	4.728
298.1	52.21	2.544	62.20	3.178	68.32	3.829	71.20	4.893
350	53.60	3.088	63.95	3.936	70.43	4.733	73.91	6.037
400	54.80	3.664	65.49	4.724	72.27	5.657	76.25	7.085
500	56.92	4.943	68.24	6.418	75.55	7.615	80.42	9.560
600	58.79	6.375	70.66	8.233	78.41	9.678	83.95	11.981
700	60.48	7.938						
800	62.04	9.613						
900	63.49	11.391						
1000	64.86	13.257						
1100	66.15	15.199						
1200	67.37	17.208						

TABLE IX. Heat capacities at constant pressure of ideal gas, cal./mole °K.

T°K	CH ₃ Br	CH ₂ Br ₂	CHBr ₃	CBr ₄	H ₂ CO	Cl ₂ CO
298.1	10.18	14.25	17.08	21.84	8.90	12.73
350	11.07	15.30	18.09	22.66	9.44	13.40
400	11.96	16.19	18.89	23.24	10.00	13.93
500	13.60	17.60	20.17	24.04	11.07	14.71
600	15.05	18.70	21.10	24.52	12.09	15.32
700	16.27				12.97	15.78
800	17.30				13.77	16.14
900	18.24				14.48	16.42
1000	19.06				15.09	
1100	19.78				15.63	
1200	20.41				16.10	
1300					16.49	
1400					16.84	
1500					17.14	

TABLE X.

T°K	H ₂ CO	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CH ₃ Cl	COCl ₂
298.1	-26.5	-14.9	-15.7	-16.1	-13.6	-50.3
350	-26.2	-13.8	-14.4	-14.5	-12.5	-49.8
400	-25.9	-12.1	-13.1	-12.9	-11.4	-49.2
500	-25.2	-10.2	-10.5	-9.9	-9.0	-48.2
600	-24.4	-7.8	-7.9	-6.7	-6.6	-47.1
700	-23.6	-5.4	-5.2		-4.0	-46.1
800	-22.8	-2.9	-2.3		-1.5	-45.0
900	-21.9				+1.2	-43.8
1000	-21.0				3.8	
1100	-20.1				6.5	
1200	-19.2				9.1	
1300	-18.3					
1400	-17.4					
1500	-16.5					

 ΔF° of formation of the gases at 1 atmos.

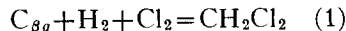
$+2\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{CH}_3\text{OH}$, $\Delta E_0^0 = -45.62$. Thus from the Newton and Dodge K_1 one has, $C_{\beta g} + \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{CO}$, $\Delta E_0^0 = -28.7$ Kcal./mole and from their K_2 , $\Delta E_0^0 = -25.2$ Kcal./mole. The mean of these two values of ΔE_0^0 is -27.0 Kcal./mole which agrees with the combustion value, obtained in the previous paragraph, within the limits of experimental error of the determination. In calculating the free energy of formation of formaldehyde we have used the unweighted mean of the three independent values of ΔE_0^0 of formation of formaldehyde, -27.2 Kcal./mole. The free energy function for oxygen was obtained from the publication of Johnston and Walker.²⁷

In Table VIII we have the free energy function and heat content for the chloro- and bromomethanes tabulated. The standard state is the usual one for statistical mechanical calculations, namely the infinitely dilute gas at 0°K. The hundred degree intervals for which the functions are given are sufficient for graphical interpolation. The units are kilocalories per mole per degree or per mole as the case may be.

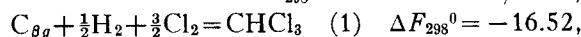
Using the Bichowsky and Rossini²⁰ values for the heats of formation of the chloromethanes one

²⁷ Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

obtains the following value for ΔE_0^0 of formation of the gaseous chloromethanes. CH_3Cl , -18.02 ; CH_2Cl_2 , -19.86 ; CHCl_3 , -22.19 ; CCl_4 , -25.10 . Combining these energies with the values of $\Delta(F^0 - E_0^0/T)$ we obtain the free energy of formation of these compounds (Table X). The vapor pressures of CH_2Cl_2 , CHCl_3 and CCl_4 are 0.570, 0.264 and 0.150 atmos., respectively.²² Thus one has,



$$\Delta F_{298}^0 = -15.25 \text{ Kcal./mole,}$$



Bichowsky and Rossini^{19, 20} from the various measurements on the equilibrium, $\text{Cl}_2 + \text{CO} = \text{Cl}_2\text{CO}$, estimate ΔH_{291}^0 to be -53.5 Kcal./mole. This corresponds to $\Delta E_0^0 = -52.7$. Using this figure for ΔE_0^0 we have calculated the free energy of formation of phosgene.

Table X contains the free energy of formation of the chloromethanes, formaldehyde and phosgene at one atmosphere.

Following other workers^{28, 29} in this field we have used the *International Critical Tables* values for the fundamental physical constants.

²⁸ Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

²⁹ Cross, J. Chem. Phys. **3**, 167 (1935).