NOMENCLATURE

A, B = van Laar constants
P = total pressure of mixture
P_i° = vapor pressure of pure component i
SS = sum of squares
x_i = mole fraction of component i in the liquid phase
γ_i = activity coefficient of component i in the liquid phase

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Thermodynamic Functions of Methane

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Standard-state thermodynamic functions for gaseous methane are reported for the temperature range 60° K. to 5000° K., taking into consideration low-temperature quantum effects, anharmonicity, centrifugal distortion, and vibration-rotation interaction.

ALTHOUGH METHANE is a thermodynamically important molecule, no tables of its thermodynamic functions appear to have been published in which the rigid-rotator, harmonic oscillator (RRHO) approximation was abandoned. The best available values (*11*) are based on an RRHO calculation performed in 1944 (*10*). Spectroscopic information on methane has increased to the point where now the higher-order corrections can be applied. This paper reports the standard state thermodynamic functions for gaseous methane from 60° K. to 5000° K., taking into consideration low-temperature quantum effects, anharmonicity (*16*), centrifugal distortion (*8*), and vibration-rotation interaction (*9*).

The functions were calculated for an ideal gas at 1 atm. pressure. The RRHO values were obtained using the Viney (*15*) rotational partition function. Correction terms were included for anharmonicity through the second order (*i.e.*, terms varying as T^2 at high temperatures). The contribution of nuclear spin was not included. Separate calculations were made for $C^{12}H_4$ and $C^{13}H_4$ using $C^{13}H_4$ frequencies and anharmonicities calculated as previously described (*7*). The maximum difference in C_p°/R between these calculations and the values obtained using $C^{12}H_4$ frequencies and anharmonicities and a mean molecular weight (based on 1.11% $C^{13}H_4$) was only 0.0002. Since this is less than the probable error introduced by uncertainties in the molecular constants, the values reported here are based on the $C^{12}H_4$ constants and the mean molecular weight. Physical-scale constants (*3*) were used with hc/k = 1.43880 cm. deg. and a translational entropy constant of −1.16552. Calculations were carried out on an IBM 7090 computer.

The molecular constants selected for this work are listed in Table I.

Because of the extreme complexity of the methane spectrum, due in large part to the high degeneracy of most bands and the resultant opportunity for various types of interaction, the selection of a suitable set of constants is difficult. This will probably be the situation for some time to come, since the finer points of the spectra of tetrahedral molecules are only now beginning to be studied in detail (*4*, *5*) and the effect of higher-order perturbations of such molecules on their thermodynamic functions

Table I. Molecular Constants of Methane

Mass = 16.04757 amu. (physical scale) (*14*)
Rotational Constants (*13*)
B_0 = 5.2406 cm.$^{-1}$
D_0 = 1.23×10^{-4} cm.$^{-1}$
σ = 12
Vibrational Constants (cm.$^{-1}$)

	$i = 1$	$i = 2$	$i = 3$	$i = 4$
ν_i (*2, 13*)	2916.7	1533.6	3018.9	1305.9
X_{1i} (*7*)	−64.6	0	−65.0	0
X_{2i}		0	−15.0	−11.2
X_{3i}			−17.5	−12.0
X_{4i}				−6.0
α_i	−0.025	−0.11	0.037	0.045

Table II. Thermodynamic Functions of Methane

T, ° K.	C_p°/R	$(H^\circ - H_0^\circ)/RT$	$-(F^\circ - H_0^\circ)/RT$	S°/R
60	4.0014	3.9693	11.9644	15.9337
80	4.0019	3.9774	13.1075	17.0849
90.67	4.0021	3.9803	13.6056	17.5859
100	4.0024	3.9823	13.9956	17.9779
111.67	4.0027	3.9844	14.4353	18.4197
120	4.0029	3.9857	14.7220	18.7077
140	4.0042	3.9882	15.3366	19.3248
160	4.0075	3.9904	15.8693	19.8597
180	4.0153	3.9927	16.3394	20.3321
200	4.0309	3.9956	16.7602	20.7559
220	4.0571	4.0000	17.1412	21.1412
240	4.0966	4.0063	17.4895	21.4958
260	4.1506	4.0152	17.8105	21.8257
273.15	4.1943	4.0227	18.0088	22.0316
280	4.2196	4.0272	18.1085	22.1357
298.15	4.2947	4.0412	18.3619	22.4030
300	4.3030	4.0428	18.3869	22.4296
320	4.3996	4.0620	18.6484	22.7104
340	4.5077	4.0850	18.8953	22.9803
360	4.6257	4.1117	19.1295	23.2412
380	4.7516	4.1420	19.3526	23.4947
400	4.8839	4.1758	19.5659	23.7417
450	5.2328	4.2737	20.0632	24.3369
500	5.5941	4.3876	20.5193	24.9069
550	5.9565	4.5138	20.9433	25.4571
600	6.3136	4.6489	21.3418	25.9907
650	6.6620	4.7904	21.7195	26.5099
700	6.9996	4.9363	22.0798	27.0160
750	7.3253	5.0847	22.4254	27.5101
800	7.6382	5.2346	22.7584	27.9930
850	7.9380	5.3849	23.0802	28.4651
900	8.2243	5.5347	23.3922	28.9270
950	8.4972	5.6835	23.6955	29.3790
1000	8.7566	5.8308	23.9908	29.8215
1050	9.0029	5.9760	24.2788	30.2548
1100	9.2363	6.1189	24.5601	30.6790
1150	9.4573	6.2593	24.8352	31.0945
1200	9.6663	6.3970	25.1045	31.5015
1300	10.0508	6.6635	25.6271	32.2906
1400	10.3944	6.9180	26.1303	33.0483
1500	10.7015	7.1601	26.6160	33.7761
1600	10.9767	7.3902	27.0855	34.4757
1700	11.2239	7.6086	27.5401	35.1487
1800	11.4469	7.8157	27.9809	35.7967
1900	11.6486	8.0122	28.4088	36.4211
2000	11.8320	8.1987	28.8246	37.0233
2100	11.9995	8.3758	29.2289	37.6047
2200	12.1531	8.5440	29.6225	38.1665
2300	12.2945	8.7040	30.0058	38.7098
2400	12.4255	8.8564	30.3795	39.2359
2500	12.5471	9.0016	30.7440	39.7456
2600	12.6607	9.1401	31.0998	40.2399
2700	12.7672	9.2725	31.4472	40.7197
2800	12.8675	9.3991	31.7867	41.1859
2900	12.9622	9.5203	32.1187	41.6390
3000	13.0521	9.6365	32.4434	42.0800
3200	13.2194	9.8553	33.0724	42.9277
3400	13.3732	10.0577	33.6761	43.7337
3600	13.5162	10.2458	34.2563	44.5021
3800	13.6507	10.4214	34.8150	45.2364
4000	13.7784	10.5860	35.3538	45.9398
4200	13.9007	10.7408	35.8741	46.6149
4400	14.0187	10.8870	36.3772	47.2642
4600	14.1333	11.0256	36.8642	47.8898
4800	14.2453	11.1573	37.3362	48.4935
5000	14.3552	11.2828	37.7943	49.0771

Table III. Contributions of Individual Terms to C_p^o/R

	298.15° K.	600° K.	1000° K.	5000° K.
RRHO Ampproximation	4.2866	6.2819	8.6352	12.6944
Anharmonicity	0.0002	0.0197	0.1026	1.5114
Centrifugal Distortion	0.0071	0.0145	0.0248	0.1661
Rot-Vib Interaction	0.0008	−0.0025	−0.0060	−0.0167
Total C_p^o/R	4.2947	6.3136	8.7566	14.3552

remains unknown. The treatment used here, however, should give a close approximation to the true thermodynamic functions and thus be a considerable improvement over the RRHO approximation.

The rotational constants obtained by Thomas and Welsh (*13*) from the fundamental ν_3 were selected as being the best available. The rotation-vibration interaction constants, defined by $B_v = B_o - \sum \alpha_i v_i$, present particular problems, among which is the probability that this definition is something of an oversimplification for spherical top molecules; we shall assume that the relationship is valid at least for the lower vibrational states. Hecht (*6*) has estimated that $\alpha_3 = 0.042$ cm.$^{-1}$, but the overtone $2\nu_3$ suggests a somewhat lower value (*4, 12*). An estimate of α_2 is available from the work of Thomas and Welsh (*13*), and Fox's (*4*) recent analysis of $2\nu_4$ gives $\alpha_4 = 0.045$ cm.$^{-1}$. No direct information is available on α_1, but a study (*1*) of the combination band $\nu_1 + \nu_4$ suggests that $\alpha_1 + \alpha_4 \sim 0.02$, giving a value for α_1 which is consistent with the shape of the Q branch of ν_1 as observed in the Raman spectrum (*13*).

The calculated values of the thermodynamic functions obtained from these data are listed in Table II. Table III indicates the values of the individual correction terms to C_p^o/R at several temperatures; the corrections to the other functions are somewhat smaller. The effect of vibration-rotation interaction is greater than the figures of Table III suggest; the apparently small contributions listed there result from fortuitous near-cancellation of the terms due to α_2 and α_4, which are the major contributors. Actually the uncertainty in the α's is the greatest source of uncertainty in these calculations; a change in α_4 (the most sensitive constant) of ± 0.01 cm.$^{-1}$, for example, will result in a change of ± 0.0090 in C_p^o/R at 1000° K.

In a recently published paper, J. Herranz and B.P. Stoicheff, *J. Mol. Spectr.* **10**, 448 (1963), have derived slightly different molecular constants from the ν_3 Raman band: $\nu_3 = 3019$, $B_o = 5.2412$, $D_o = 1.12 \times 10^{-4}$, $\alpha_3 = 0.0416$ cm.$^{-1}$. We have recalculated the thermodynamic functions using these values in place of the corresponding constants in Table I, and find that C_p^o/R is raised 0.02% at 1000° K. and 0.08% at 5000° K.; the effect on the other functions is even less.

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