South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

MET 320 Final Exam Dec 21, 2007
Closed Note and Book No Calculators

Constants:
R = 1.987 cal/K•gmole = 8.31 J/K•gmole
F = 23,060 cal/volt•gram equivalent = 96,259 Joule/volt•gram equivalent

1. Show on the attached Ellingham Diagram
   a) The pressure of O2 in equilibrium with Si and SiO2 at 1300°C

   b) The H2/H2O ratio in equilibrium with Si and SiO2 at 1300°C

   c) The CO/CO2 ratio in equilibrium with Si and SiO2 at 1300°C

   d) Estimate the for one gram mole of Mg
      i) Heat of Fusion

      ii) Heat of Vaporization.

2. Find the adiabatic flame temperature for the combustion of CH_4 with pure O_2. The O_2 and the CH_4 start at 298°K. Use the data provided below only.

$$CH_4\,(g) + 2\,O_2(g) = CO_2\,(g) + 2\,H_2O(g)$$

Species	Heats of Formation (calories/g mole at 298°K)	C_p (cal/ gmole °K)
$CH_4(g)$	see JANAF	
$H_2O(g)$	see JANAF	
$CO_2(g)$	see JANAF	
$O_2(g)$		8.6
$N_2(g)$		7.0

3. **CaO-Al_2O_3-SiO_2 (C-A-S) Ternary Phase Diagram**
   Show all constructions on the diagram.
   a) What is the bulk composition of the composition marked "**1**",
      i) Percent SiO_2 = _____

      ii) Percent CaO = _____

   b) For the bulk composition marked "**2**", what is the 1st crystal to appear upon cooling?

   c) For the bulk composition marked "**3**", what are the final 3 crystals?

   d) For the bulk composition marked "**4**", what percent liquid is present at 1400 °C

4. Pure, liquid $MgCl_2$ at 1100 K is to undergo electrolysis to form Cl_2 gas at a pressure of 0.1 ATM and pure, liquid magnesium. What cell potential is needed? Use JANAF data.

5. One mole of an ideal gas at 2 atm and 500 K are adiabatically compressed to 10 atm.
   a) What is the final temperature?

   b) How much heat was required?

   c) How much work was required?

6. What is the maximum amount of work that could be obtained from 1000 BTU's of heat from a boiler at 1000 K if the coldest heat sink available is at 400 K?

7. A railroad tanker has wrecked and caught fire. There are sealed canisters of liquid ammonia, NH_3, near the fire in a pool of boiling water at 370 K. What is the pressure of NH_3 in the bottles? The heat of vaporization of ammonia is 21,725 J/gmole and boils at –33 ºC.

8. Would a gas with a partial pressure of Cl_2 of 10^{-6} atm react with liquid Na to form liquid NaCl at 1000 K? Show your work.

$$Na_{(l)} + 0.5\ Cl_{2(g)} = NaCl_{(l)} \qquad \Delta G° = -375{,}232 + 58.508T \text{ J/gmole}$$

9. How many degrees of freedom are there in a system consisting of $MgO_{(s)}$, $MgCO_{3(s)}$, $CaO_{(s)}$, $CaCO_{3(s)}$, $CO_{2(g)}$, and $N_{2(g)}$?
The oxide and carbonate are pure (i.e. - insoluble in one another).
The gases, of course, form a gas mixture.

10. Complete the Fundamental Equations for a closed system

$dU = TdS - PdV$

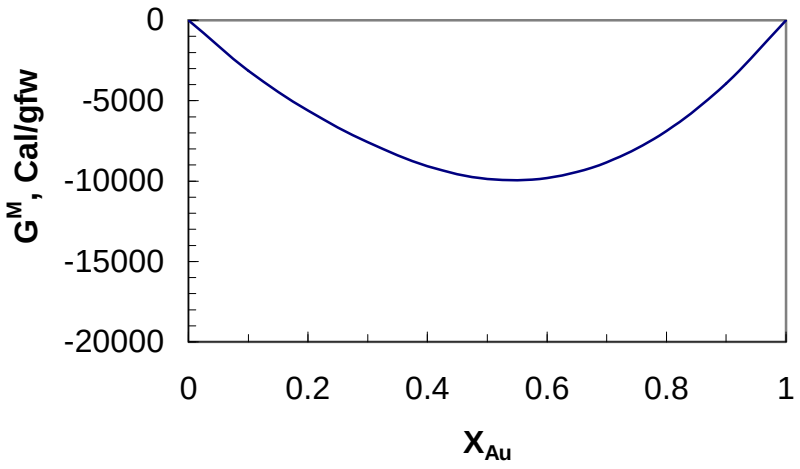
$dH =$

$dA =$

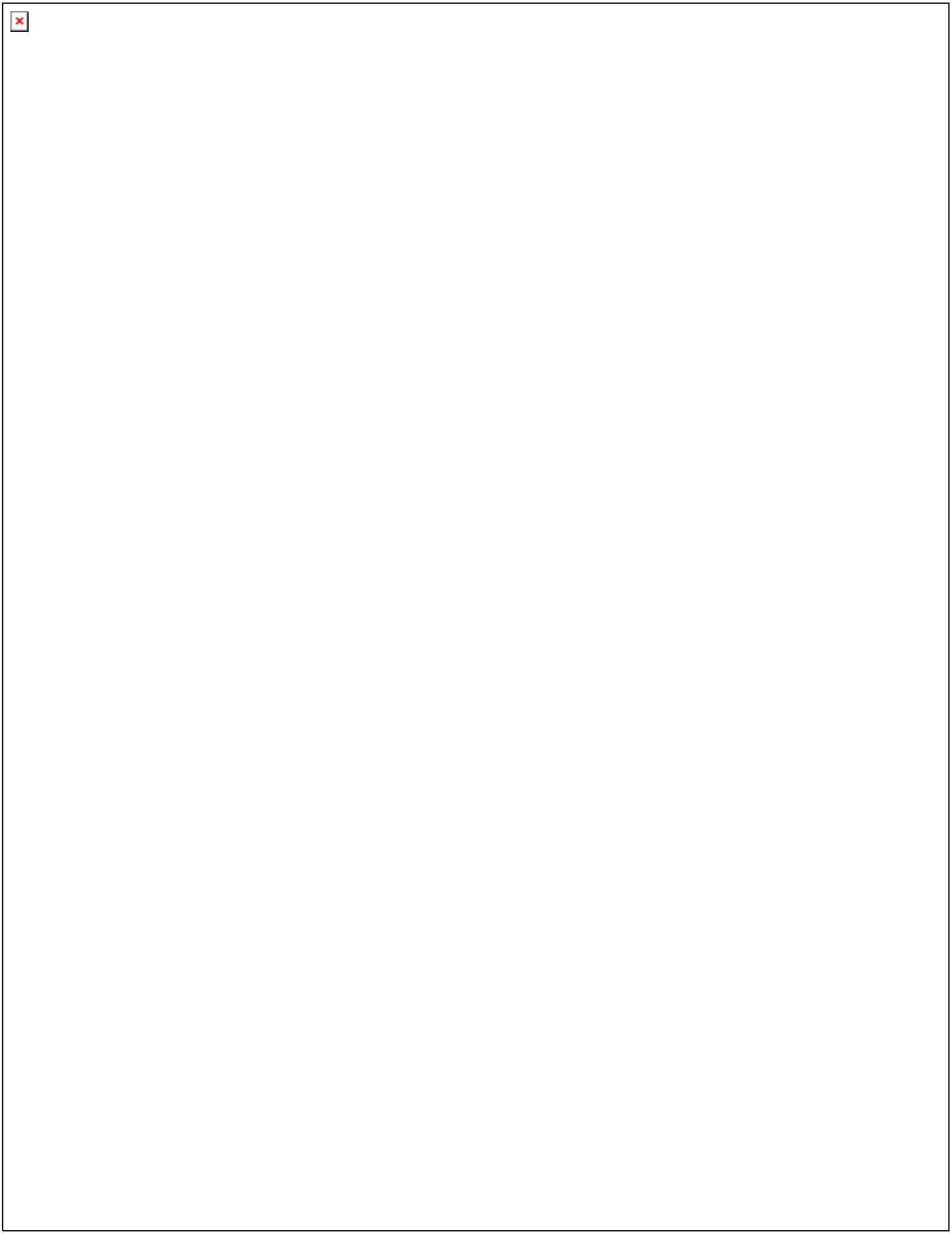
$dG =$

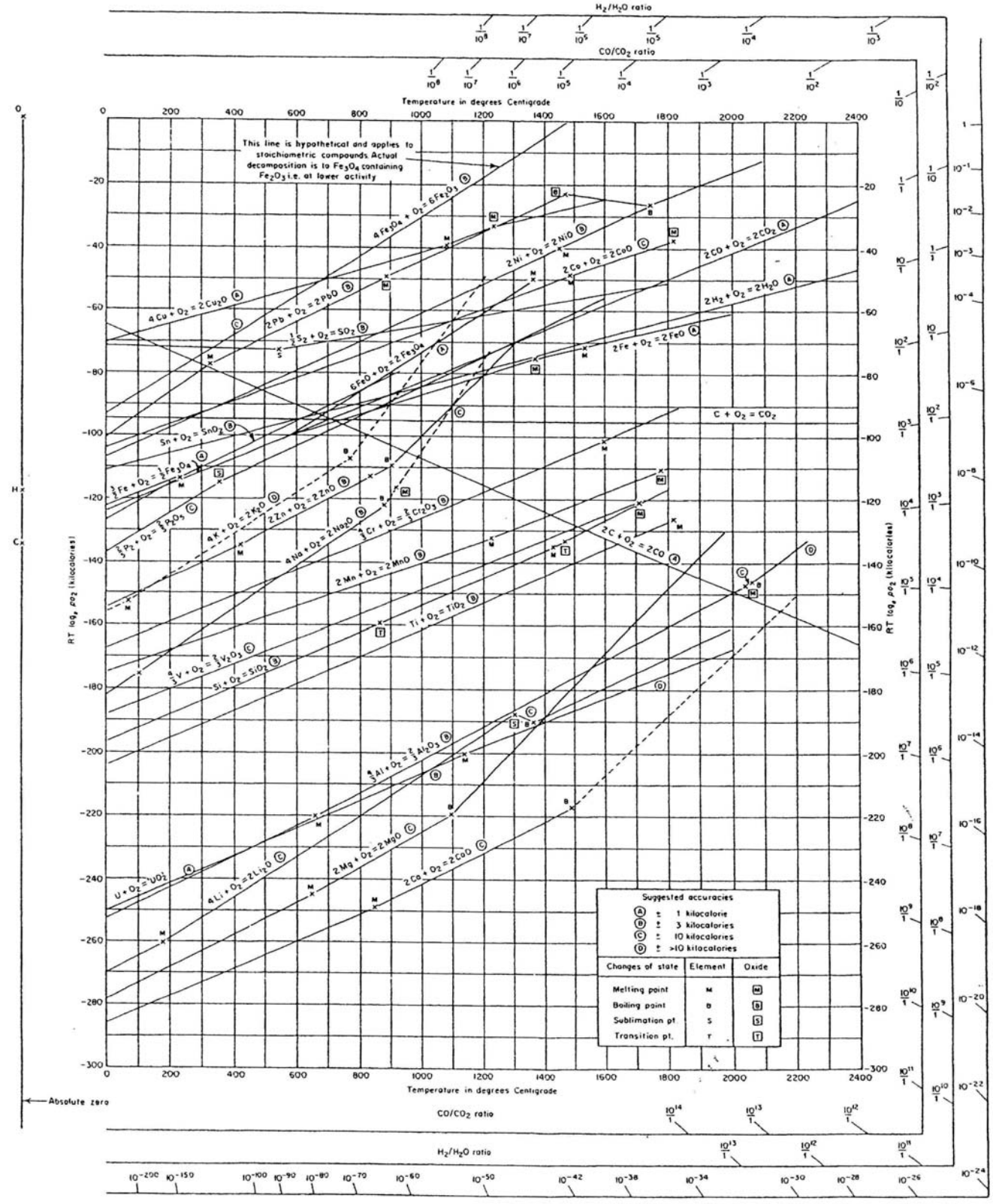
11. Find the activity of Au in a liquid Au-Cu alloy at 1338 K that is 60 atomic percent Au from the following data:

X_{Au}	G^M
0	0
0.1	-3145
0.2	-5605
0.3	-7586
0.4	-9066
0.5	-9875
0.6	-9817
0.7	-8830
0.8	-6878
0.9	-3950
1	0



Gibbs Energy of Mixing for theLiquid Al-Au System at 1338 K





9.2. *Based on a diagram supplied by the British Iron & Steel Research Association*

Scratch Paper - Discard

Methane (CH_4)

(Ideal Gas) Mol. Wt. = 16.043

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.396	- 15.991	- 15.991	INFINITE
100	7.949	35.706	51.716	- 1.401	- 16.728	- 15.400	33.656
200	8.001	41.222	46.247	- .805	- 17.216	- 13.909	15.198
298	8.518	44.490	44.490	.000	- 17.895	- 12.145	8.902
300	8.535	44.543	44.490	.016	- 17.909	- 12.110	8.822
400	9.680	47.144	44.837	.923	- 18.636	- 10.066	5.500
500	11.076	49.453	45.533	1.960	- 19.316	- 7.845	3.429
600	12.483	51.597	46.367	3.138	- 19.916	- 5.493	2.001
700	13.813	53.622	47.260	4.454	- 20.429	- 3.046	.951
800	15.041	55.548	48.176	5.897	- 20.857	- .533	.146
900	16.157	57.385	49.098	7.458	- 21.207	2.029	+ .493
1000	17.160	59.141	50.016	9.125	- 21.482	4.625	+ 1.011
1100	18.052	60.819	50.922	10.887	- 21.696	7.247	+ 1.440
1200	18.842	62.424	51.814	12.732	- 21.854	9.887	+ 1.801
1300	19.538	63.960	52.690	14.652	- 21.971	12.535	+ 2.107
1400	20.150	65.431	53.548	16.637	- 22.050	15.195	+ 2.372
1500	20.688	66.840	54.387	18.679	- 22.104	17.859	+ 2.602
1600	21.161	68.191	55.208	20.772	- 22.137	20.520	+ 2.803
1700	21.579	69.486	56.010	22.910	- 22.148	23.189	+ 2.981
1800	21.947	70.730	56.794	25.086	- 22.144	25.854	+ 3.139
1900	22.273	71.926	57.559	27.298	- 22.127	28.522	+ 3.281
2000	22.562	73.076	58.306	29.540	- 22.099	31.187	+ 3.408
2100	22.820	74.183	59.036	31.809	- 22.065	33.851	+ 3.523
2200	23.050	75.250	59.749	34.103	- 22.026	36.511	+ 3.627
2300	23.256	76.279	60.445	36.418	- 21.981	39.173	+ 3.722
2400	23.441	77.273	61.126	38.753	- 21.935	41.833	+ 3.809
2500	23.608	78.233	61.791	41.106	- 21.888	44.483	+ 3.889
2600	23.758	79.162	62.441	43.474	- 21.839	47.141	+ 3.962
2700	23.894	80.062	63.077	45.857	- 21.790	49.791	+ 4.030
2800	24.018	80.933	63.700	48.253	- 21.741	52.440	+ 4.093
2900	24.131	81.778	64.309	50.660	- 21.694	55.093	+ 4.152
3000	24.233	82.597	64.905	53.079	- 21.649	57.736	+ 4.206
3100	24.327	83.394	65.488	55.507	- 21.602	60.381	+ 4.257
3200	24.413	84.167	66.060	57.944	- 21.561	63.026	+ 4.304
3300	24.493	84.920	66.620	60.389	- 21.524	65.669	+ 4.349
3400	24.565	85.652	67.169	62.842	- 21.488	68.309	+ 4.391
3500	24.633	86.365	67.707	65.302	- 21.459	70.951	+ 4.430
3600	24.695	87.060	68.235	67.768	- 21.433	73.589	+ 4.467
3700	24.752	87.737	68.753	70.241	- 21.414	76.231	+ 4.503
3800	24.806	88.398	69.262	72.719	- 21.397	78.872	+ 4.536
3900	24.855	89.043	69.761	75.202	- 21.389	81.511	+ 4.568
4000	24.901	89.673	70.251	77.690	- 21.386	84.150	+ 4.598
4100	24.944	90.288	70.732	80.182	- 21.387	86.785	+ 4.626
4200	24.984	90.890	71.205	82.678	- 21.397	89.429	+ 4.653
4300	25.022	91.478	71.669	85.179	- 21.412	92.063	+ 4.679
4400	25.057	92.054	72.126	87.683	- 21.434	94.700	+ 4.704
4500	25.090	92.617	72.575	90.190	- 21.463	97.335	+ 4.727
4600	25.121	93.169	73.017	92.701	- 21.498	99.983	+ 4.750
4700	25.150	93.710	73.452	95.214	- 21.540	102.625	+ 4.772
4800	25.177	94.240	73.879	97.730	- 21.589	105.268	+ 4.793
4900	25.203	94.759	74.300	100.249	- 21.644	107.912	+ 4.813
5000	25.227	95.268	74.714	102.771	- 21.706	110.552	+ 4.832
5100	25.250	95.768	75.122	105.295	- 21.777	113.198	+ 4.851
5200	25.272	96.259	75.524	107.821	- 21.853	115.844	+ 4.869
5300	25.292	96.740	75.920	110.349	- 21.937	118.501	+ 4.886
5400	25.311	97.213	76.310	112.879	- 22.029	121.145	+ 4.903
5500	25.330	97.678	76.694	115.411	- 22.128	123.799	+ 4.919
5600	25.347	98.134	77.073	117.945	- 22.234	126.449	+ 4.935
5700	25.364	98.583	77.446	120.481	- 22.348	129.106	+ 4.950
5800	25.379	99.024	77.814	123.018	- 22.469	131.762	+ 4.965
5900	25.394	99.458	78.178	125.557	- 22.598	134.428	+ 4.979
6000	25.409	99.885	78.536	128.097	- 22.732	137.081	+ 4.993

March 31, 1961

METHANE (CH_4) (IDEAL GAS) MOL. WT. = 16.043

ΔH°_{f0} = -15.99 ± 0.08 kcal. mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = -17.895 ± 0.08 kcal. mole^{-1}

Point Group T_d $S_{298.15}$ = 44.48 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
2916.5 (1)
1534.0 (2)
3018.7 (3)
1306 (3)

Bond Lengths and Angles ∢ H-C-H = 109° 28' C-H = 1.091 ± 0.002 Å

Moments of Inertia $I_A = I_B = I_C = 5.313 \times 10^{-40}$ g. cm.^{2}

Heat of Formation

F. D. Rossini, J. Research Nat. Bur. Standards 6, 37 (1931) measured the heat of combustion of methane gas. His value at 298.15°K was corrected to the presently accepted molecular weight of water. The heat of formation was calculated using -68.3174 and -94.0540 kcal. mole^{-1} for the heat of formation of $H_2O(l)$ and $CO_2(g)$ respectively.

Heat Capacities and Entropies

D. P. Stevenson and J. A. Ibers, J. Chem. Phys. 33, 762 (1960), calculated the bond distance from an analysis of available spectroscopic data. Vibrational frequencies listed by L. H. Jones and R. S. McDowell, J. Mol. Spect. 3, 632 (1959), are consistent with their results of a force constant calculation.

Carbon Dioxide (CO_2)

(Ideal Gas) Mol. Wt. = 44.00995

T. °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.238	- 93.965	- 93.965	INFINITE
100	6.981	42.758	58.188	- 1.543	- 93.997	- 94.100	205.645
200	7.734	47.789	51.849	- .816	- 94.028	- 94.191	102.922
298	8.874	51.072	51.072	.000	- 94.054	- 94.265	69.095
300	8.896	51.127	51.072	.016	- 94.055	- 94.267	68.670
400	9.877	53.830	51.434	.958	- 94.070	- 94.335	51.540
500	10.666	56.122	52.148	1.987	- 94.091	- 94.399	41.260
600	11.310	58.126	52.981	3.087	- 94.124	- 94.458	34.405
700	11.846	59.910	53.845	4.245	- 94.169	- 94.510	29.506
800	12.293	61.522	54.706	5.453	- 94.218	- 94.556	25.830
900	12.667	62.992	55.546	6.702	- 94.270	- 94.596	22.970
1000	12.980	64.344	56.359	7.984	- 94.321	- 94.628	20.680
1100	13.243	65.594	57.143	9.296	- 94.371	- 94.658	18.806
1200	13.466	66.756	57.896	10.632	- 94.419	- 94.681	17.243
1300	13.656	67.841	58.620	11.988	- 94.469	- 94.701	15.920
1400	13.815	68.859	59.315	13.362	- 94.515	- 94.716	14.785
1500	13.953	69.817	59.984	14.750	- 94.562	- 94.728	13.801
1600	14.074	70.722	60.627	16.152	- 94.607	- 94.739	12.940
1700	14.177	71.579	61.246	17.565	- 94.650	- 94.746	12.180
1800	14.269	72.391	61.843	18.987	- 94.696	- 94.750	11.504
1900	14.352	73.165	62.418	20.418	- 94.742	- 94.751	10.898
2000	14.424	73.903	62.974	21.857	- 94.788	- 94.752	10.353
2100	14.489	74.608	63.512	23.303	- 94.834	- 94.746	9.860
2200	14.547	75.284	64.031	24.755	- 94.885	- 94.744	9.411
2300	14.600	75.931	64.535	26.212	- 94.936	- 94.735	9.001
2400	14.648	76.554	65.023	27.674	- 94.991	- 94.724	8.625
2500	14.692	77.153	65.496	29.141	- 95.048	- 94.714	8.280
2600	14.734	77.730	65.956	30.613	- 95.107	- 94.698	7.960
2700	14.771	78.286	66.402	32.088	- 95.170	- 94.683	7.664
2800	14.807	78.826	66.836	33.567	- 95.235	- 94.662	7.388
2900	14.841	79.344	67.255	35.049	- 95.305	- 94.639	7.132
3000	14.873	79.848	67.670	36.534	- 95.377	- 94.615	6.892
3100	14.902	80.336	68.071	38.024	- 95.451	- 94.587	6.668
3200	14.930	80.810	68.461	39.515	- 95.530	- 94.560	6.458
3300	14.956	81.270	68.843	41.010	- 95.611	- 94.531	6.260
3400	14.982	81.717	69.215	42.507	- 95.696	- 94.495	6.074
3500	15.006	82.151	69.578	44.006	- 95.784	- 94.462	5.898
3600	15.030	82.574	69.933	45.508	- 95.874	- 94.421	5.732
3700	15.053	82.986	70.280	47.012	- 95.968	- 94.379	5.574
3800	15.075	83.388	70.620	48.518	- 96.064	- 94.331	5.425
3900	15.097	83.780	70.953	50.027	- 96.162	- 94.286	5.283
4000	15.119	84.162	71.278	51.538	- 96.263	- 94.237	5.149
4100	15.139	84.536	71.597	53.051	- 96.367	- 94.186	5.020
4200	15.159	84.901	71.909	54.566	- 96.473	- 94.130	4.898
4300	15.179	85.258	72.216	56.082	- 96.583	- 94.072	4.781
4400	15.197	85.607	72.516	57.601	- 96.694	- 94.015	4.670
4500	15.216	85.949	72.811	59.122	- 96.807	- 93.954	4.563
4600	15.234	86.284	73.100	60.644	- 96.923	- 93.885	4.460
4700	15.254	86.611	73.384	62.169	- 97.040	- 93.818	4.362
4800	15.272	86.933	73.663	63.695	- 97.160	- 93.746	4.268
4900	15.290	87.248	73.937	65.223	- 97.281	- 93.678	4.178
5000	15.306	87.557	74.206	66.753	- 97.404	- 93.603	4.091
5100	15.327	87.860	74.471	68.285	- 97.530	- 93.528	4.008
5200	15.349	88.158	74.731	69.819	- 97.656	- 93.450	3.927
5300	15.371	88.451	74.988	71.355	- 97.783	- 93.361	3.850
5400	15.393	88.738	75.239	72.893	- 97.912	- 93.280	3.775
5500	15.415	89.021	75.488	74.433	- 98.042	- 93.190	3.703
5600	15.437	89.299	75.732	75.976	- 98.173	- 93.104	3.633
5700	15.459	89.572	75.972	77.521	- 98.305	- 93.017	3.566
5800	15.481	89.841	76.209	79.068	- 98.438	- 92.918	3.501
5900	15.503	90.106	76.442	80.617	- 98.572	- 92.820	3.438
6000	15.525	90.367	76.672	82.168	- 98.707	- 92.724	3.377

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON DIOXIDE (CO_2) (IDEAL GAS) MOL. WT. = 44.00995

Point Group $D_{\infty h}$

$\Delta H_{f\ 0}^\circ = -93.965 \pm 0.011$ kcal. mole^{-1}

$S^\circ_{298.15} = 51.07 \pm 0.03$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -94.054 \pm 0.011$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å

Bond Angle: O-C-O = 180°

$\sigma = 2$

Rotational Constant: $B_o = 0.39038$ cm.$^{-1}$

Heat of Formation.

The enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of the reaction C(c, graphite) + $O_2(g)$ = $CO_2(g)$ has been measured by F. H. Dewey and D. R. Harper, J. Res. Natl. Bur. Std. 21, 457 (1938), R. S. Jessup, ibid. 21, 491 (1938), and E. J. Prosen and F. D. Rossini, ibid., 33, 439 (1944). Based on these data, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $CO_2(g)$ was reported to be -94.0518 ± 0.0108 kcal. mole^{-1}, using molecular weight of CO_2 = 44.010, by E. J. Prosen, R. S. Jessup and F. D. Rossini, J. Research Natl. Bur. Standards 33, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole^{-1}, based on molecular weight of CO_2 = 44.011, for internal consistency.

Heat Capacity and Entropy.

The functions adopted here were obtained from H. W. Woolley, J. Research Nat. Bur. Standards 52, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., J. Chem. Phys. 30, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtoy, Mem. soc. roy. Liege 18, 496 (1957) and V. R. Stull, F. J. Wyatt and G. N. Plass, J. Chem. Phys. 37, 1442 (1962). The high-resolution infrared spectrum of O^{18} - enriched CO_2 was examined in the region 5400-1620 cm.$^{-1}$, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.$^{-1}$ by C. V. Berney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B_o, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B_e which was derived from B_o, using $B_e - B_o = 0.0011$ cm.$^{-1}$ given in G. Herzberg, loc. cit. The principal moment of inertia is $I = 7.1495 \times 10^{-39}$ g. cm.^{2}

Heat capacities of $CO_2(g)$ at high pressures were reported by M. P. Vukalovich, V. V. Altunin and A. N. Gureev, Teploenergetika, 12 (7), 58 (1965); K. Krueger, Ver. Deut. Ingr. Z., 106 (32) 1620 (1964), and M. P. Vukalovich and A. N. Gureev, Teploenergetika, 11 (8), 80 (1964).

Magnesium Dichloride ($MgCl_2$)

(Liquid) Mol. Wt. = 95.218

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	17.060	30.949	30.949	.000	- 143.779	- 134.789	98.798
300	17.088	31.055	30.949	.032	- 143.773	- 134.733	98.148
400	18.095	36.123	31.433	1.796	- 143.453	- 131.768	71.991
500	18.677	40.228	32.955	3.636	- 143.108	- 128.884	56.332
600	19.090	43.634	34.459	5.505	- 142.777	- 126.072	45.919
700	22.000	46.807	35.995	7.569	- 142.284	- 123.321	38.501
800	22.000	49.745	37.534	9.769	- 141.695	- 120.654	32.959
900	22.000	52.336	39.038	11.969	- 141.146	- 118.056	28.667
1000	22.000	54.654	40.485	14.169	- 142.759	- 115.337	25.206
1100	22.000	56.751	41.870	16.369	- 142.258	- 112.621	22.375
1200	22.000	58.665	43.191	18.569	- 141.785	- 109.948	20.023
1300	22.000	60.426	44.450	20.769	- 141.340	- 107.313	18.040
1400	22.000	62.056	45.650	22.969	- 171.288	- 104.231	16.270
1500	22.000	63.574	46.795	25.169	- 170.491	- 99.469	14.492
1600	22.000	64.994	47.889	27.369	- 169.696	- 94.762	12.943
1700	22.000	66.328	48.935	29.569	- 168.902	- 90.101	11.583
1800	22.000	67.585	49.936	31.769	- 168.110	- 85.489	10.379
1900	22.000	68.775	50.897	33.969	- 167.318	- 80.920	9.307
2000	22.000	69.903	51.819	36.169	- 166.530	- 76.392	8.347
2100	22.000	70.977	52.706	38.369	- 165.742	- 71.908	7.483
2200	22.000	72.000	53.560	40.569	- 164.957	- 67.456	6.701
2300	22.000	72.978	54.383	42.769	- 164.173	- 63.040	5.990
2400	22.000	73.914	55.177	44.969	- 163.391	- 58.660	5.341
2500	22.000	74.812	55.945	47.169	- 162.613	- 54.313	4.748
2600	22.000	75.675	56.687	49.369	- 161.836	- 49.995	4.202
2700	22.000	76.506	57.406	51.569	- 161.063	- 45.711	3.700
2800	22.000	77.306	58.103	53.769	- 160.293	- 41.453	3.235
2900	22.000	78.078	58.778	55.969	- 159.526	- 37.222	2.805
3000	22.000	78.824	59.434	58.169	- 158.764	- 33.019	2.405

Dec. 31, 1960; Dec. 31, 1965

Cl_2Mg

MAGNESIUM DICHLORIDE ($MgCl_2$) (LIQUID) MOL. WT. = 95.218

$S^\circ_{298.15}$ = 30.949 cal. deg.$^{-1}$ mole^{-1}

T_m = 987°K.

T_b = [1710]°K.

ΔH_f° 298.15 = -143.779 kcal. mole^{-1}

ΔH_m° = 10.30 ± 0.05 kcal. mole^{-1}

ΔH_v° = [37.34] kcal. mole^{-1}

Heat of Formation.

ΔH_f° 298.15(l) was calculated from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between $H^\circ_{T_m}-H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A constant C_p(l) = 22.0 cal. deg.$^{-1}$ mole^{-1} over the temperature range 1006-1428°K. is from the high temperature heat content data of G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). This constant value was assumed to hold from an assumed glass transition of 660°K. to 3000°K. C_p(l) below 660°K. is taken to be that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See $MgCl_2$(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction $MgCl_2(l) = MgCl_2(g)$ approaches zero. The difference between ΔH_f° for $MgCl_2$(l) and $MgCl_2$(g) at T_b is ΔH_v°.

Cl_2Mg

anium Tetrachloride ($TiCl_4$)

eal Gas) GFW = 189.712

, °K	Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	- 5.166	- 182.026	- 182.026	INFINITE
100	16.117	63.412	103.421	- 4.001	- 182.387	- 179.501	392.299
200	20.582	76.098	84.822	- 2.145	- 182.441	- 176.584	192.962
298	22.852	84.793	84.793	.000	- 182.400	- 173.721	127.341
300	22.881	84.935	84.794	.042	- 182.399	- 173.667	126.516
400	24.006	91.690	85.707	2.393	- 182.326	- 170.767	93.303
500	24.610	97.118	87.464	4.827	- 182.244	- 167.886	73.383
600	24.962	101.439	89.461	7.307	- 182.168	- 165.022	60.109
700	25.183	105.504	91.483	9.815	- 182.102	- 162.171	50.632
800	25.330	108.877	93.451	12.341	- 182.056	- 159.328	43.526
900	25.433	111.867	95.334	14.879	- 182.036	- 156.486	38.000
1000	25.507	114.551	97.124	17.427	- 182.040	- 153.650	33.580
1100	25.563	116.985	98.821	19.980	- 182.070	- 150.808	29.963
1200	25.605	119.211	100.428	22.539	- 183.063	- 147.927	26.941
1300	25.639	121.262	101.953	25.101	- 183.019	- 145.061	24.377
1400	25.665	123.163	103.401	27.666	- 182.991	- 142.078	22.179
1500	25.686	124.934	104.776	30.234	- 182.980	- 139.156	20.275
1600	25.704	126.592	106.090	32.803	- 182.990	- 136.233	18.609
1700	25.719	128.151	107.343	35.375	- 183.019	- 133.308	17.138
1800	25.731	129.622	108.540	37.947	- 183.074	- 130.385	15.831
1900	25.741	131.013	109.686	40.521	- 183.151	- 127.453	14.660
2000	25.750	132.334	110.786	43.095	- 187.705	- 124.366	13.590
2100	25.758	133.590	111.842	45.671	- 187.809	- 121.196	12.613
2200	25.765	134.789	112.856	48.247	- 187.919	- 118.024	11.725
2300	25.770	135.934	113.837	50.824	- 188.030	- 114.842	10.912
2400	25.776	137.031	114.781	53.401	- 188.145	- 111.657	10.160
2500	25.780	138.083	115.692	55.979	- 188.265	- 108.466	9.462
2600	25.784	139.094	116.573	58.557	- 188.387	- 105.274	8.849
2700	25.788	140.068	117.425	61.135	- 188.515	- 102.076	8.262
2800	25.791	141.006	118.250	63.714	- 188.648	- 98.870	7.717
2900	25.794	141.911	119.051	66.294	- 188.784	- 95.661	7.204
3000	25.796	142.785	119.827	68.873	- 188.927	- 92.450	6.735
3100	25.799	143.631	120.582	71.453	- 189.075	- 89.230	6.291
3200	25.801	144.450	121.315	74.033	- 189.229	- 86.010	5.874
3300	25.803	145.244	122.028	76.613	- 189.389	- 82.779	5.482
3400	25.804	146.014	122.722	79.193	- 189.553	- 79.543	5.113
3500	25.806	146.762	123.398	81.774	- 189.724	- 76.311	4.765
3600	25.807	147.489	124.056	84.355	- 291.525	- 72.802	4.420
3700	25.809	148.197	124.700	86.935	- 291.679	- 66.724	3.941
3800	25.810	148.885	125.328	89.516	- 291.849	- 60.648	3.488
3900	25.811	149.555	125.940	92.097	- 292.038	- 54.556	3.057
4000	25.812	150.209	126.539	94.679	- 292.245	- 48.464	2.648
4100	25.813	150.846	127.124	97.260	- 292.466	- 42.369	2.258
4200	25.814	151.468	127.696	99.841	- 292.709	- 36.270	1.887
4300	25.815	152.076	128.256	102.423	- 292.963	- 30.163	1.533
4400	25.816	152.669	128.804	105.004	- 293.233	- 24.041	1.194
4500	25.817	153.249	129.341	107.586	- 293.517	- 17.925	.871
4600	25.817	153.817	129.867	110.168	- 293.811	- 11.793	.560
4700	25.818	154.372	130.383	112.749	- 294.120	- 5.657	.263
4800	25.819	154.916	130.888	115.331	- 294.440	.480	- .022
4900	25.819	155.448	131.384	117.913	- 294.771	6.629	- .296
5000	25.820	155.969	131.870	120.495	- 295.110	12.783	- .559
5100	25.820	156.481	132.346	123.077	- 295.457	18.949	- .812
5200	25.821	156.982	132.817	125.659	- 295.814	25.119	- 1.056
5300	25.821	157.474	133.276	128.241	- 296.180	31.286	- 1.290
5400	25.822	157.957	133.730	130.823	- 296.553	37.472	- 1.517
5500	25.822	158.431	134.175	133.406	- 296.930	43.666	- 1.735
5600	25.823	158.896	134.612	135.988	- 297.315	49.853	- 1.946
5700	25.823	159.353	135.042	138.570	- 297.706	56.054	- 2.149
5800	25.823	159.802	135.465	141.152	- 298.101	62.271	- 2.346
5900	25.824	160.243	135.882	143.735	- 298.501	68.483	- 2.537
6000	25.824	160.677	136.291	146.317	- 298.906	74.706	- 2.721

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE ($TiCl_4$) (IDEAL GAS) GFW = 189.712

Point Group T_d

ΔHf°_0 = -182.0 ± 0.9 kcal/mol

S°_{298} = 84.8 ± 0.7 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -182.4 ± 0.9 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
388 (1)	498.5 (3)
111 (2)	131 (3)

Bond Distance: Ti-Cl = 2.185 Å

Bond Angle: Cl-Ti-Cl = 109° 28'

σ = 12

Product of the Moments of Inertia: $I_A I_B I_C = 4.2092 \times 10^{-112}$ g^3 cm^6

Heat of Formation

The heat of formation, ΔHf°_{298}, of $TiCl_4(g)$ and $TiCl_4(\ell)$ has been measured by several investigators. The results of these measurements are as follows.

Investigators	Method	Reaction	ΔHf°_{298}, kcal/mol $TiCl_4(\ell)$	ΔHf°_{298}, kcal/mol $TiCl_4(g)$
Johnson et al. (1959) (1)	Calorimetric	$Ti(c)+2Cl_2(g) = TiCl_4(g)$	(-192.2)	-182.4±0.7
Farber and Darnell (1955) (2)	Equilibrium	$TiO_2(c)+4HCl(g) = TiCl_4(g)+2H_2O(g)$	(-192.7)	-182.9±0.5
Skinner and Ruehrwein (1955) (3)	Calorimetric	$Ti(c)+xCl_2(g) = [TiCl_4+(x-2)Cl_2]$ soln	-190.3±3.0	(-180.5)
Gross et al.(1957) (4)	Calorimetric	$Ti(c)+xCl_2(\ell) = [TiCl_4+(x-2)Cl_2]$ soln	-191.5±0.3	(-181.7)
Krieve et al. (1956) (5)	Calorimetric	$Ti(c)+xCl_2(g) = [TiCl_4+(x-2)Cl_2]$ soln	-190.0±0.4	(-180.2)
Thomsen (1882) (6)		$TiCl_4(\ell)+2H_2O(\ell) = 4HCl_{(0.002\ m)}+TiO_2(c)$	-194.5	(-184.7)

The chosen value of ΔHf°_{298} is that reported by Johnson et al. (1). This investigation has the advantage of being independent of the heat of vaporization of chlorine and any heats of solution in deriving the value of the heat of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura et al. (7). The tetrahedral structure was established by the Raman work of Bhagavantam (8). The vibrational frequencies determined from the infrared and Raman spectra of $TiCl_4$ by Hawkins and Carpenter (9) are adjusted downward 8 cm^{-1} for ν_2 and ν_4 so that the heats of vaporization determined by both second and third law methods are in agreement. See $TiCl_4(\ell)$ table for details. The principal moments of inertia are: $I_A = I_B = I_C = 74.943 \times 10^{-39}$ g cm^2.

References

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9. N. J. Hawkins and D. R. Carpenter, J. Chem. Phys. 23, 1700 (1955).

Water (H_2O)

(Ideal Gas) Mol. Wt. = 18.016

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.367	- 57.103	- 57.103	INFINITE
100	7.961	36.396	52.202	- 1.581	- 57.433	- 56.557	123.600
200	7.964	41.916	45.837	- .788	- 57.579	- 55.635	60.792
298	8.025	45.106	45.106	.000	- 57.798	- 54.636	40.048
300	8.027	45.155	45.106	.015	- 57.803	- 54.617	39.786
400	8.186	47.484	45.422	.825	- 58.042	- 53.519	29.240
500	8.415	49.334	46.026	1.654	- 58.277	- 52.361	22.886
600	8.676	50.891	46.710	2.509	- 58.500	- 51.156	18.633
700	8.954	52.249	47.406	3.390	- 58.710	- 49.915	15.583
800	9.246	53.468	48.089	4.300	- 58.905	- 48.646	13.289
900	9.547	54.570	48.749	5.240	- 59.084	- 47.352	11.498
1000	9.851	55.592	49.382	6.209	- 59.246	- 46.040	10.062
1100	10.152	56.545	49.991	7.210	- 59.391	- 44.712	8.883
1200	10.444	57.441	50.575	8.240	- 59.519	- 43.371	7.899
1300	10.723	58.288	51.136	9.298	- 59.634	- 42.022	7.064
1400	10.987	59.092	51.675	10.384	- 59.734	- 40.663	6.347
1500	11.233	59.859	52.196	11.495	- 59.824	- 39.297	5.725
1600	11.462	60.591	52.698	12.630	- 59.906	- 37.927	5.180
1700	11.674	61.293	53.183	13.787	- 59.977	- 36.549	4.699
1800	11.869	61.965	53.652	14.964	- 60.041	- 35.170	4.270
1900	12.048	62.612	54.107	16.160	- 60.099	- 33.786	3.886
2000	12.214	63.234	54.548	17.373	- 60.150	- 32.401	3.540
2100	12.366	63.838	54.976	18.602	- 60.198	- 31.012	3.227
2200	12.505	64.412	55.392	19.846	- 60.242	- 29.621	2.942
2300	12.634	64.971	55.796	21.103	- 60.282	- 28.229	2.682
2400	12.753	65.511	56.190	22.372	- 60.321	- 26.832	2.443
2500	12.863	66.034	56.573	23.653	- 60.359	- 25.439	2.224
2600	12.965	66.541	56.947	24.945	- 60.393	- 24.040	2.021
2700	13.059	67.032	57.311	26.246	- 60.428	- 22.641	1.833
2800	13.146	67.508	57.667	27.556	- 60.462	- 21.242	1.658
2900	13.226	67.971	58.014	28.875	- 60.496	- 19.838	1.495
3000	13.304	68.421	58.354	30.201	- 60.530	- 18.438	1.343
3100	13.374	68.858	58.685	31.535	- 60.562	- 17.034	1.201
3200	13.441	69.284	59.010	32.876	- 60.596	- 15.630	1.067
3300	13.503	69.698	59.328	34.223	- 60.631	- 14.223	.942
3400	13.562	70.102	59.639	35.577	- 60.666	- 12.818	.824
3500	13.617	70.496	59.943	36.936	- 60.703	- 11.409	.712
3600	13.669	70.881	60.242	38.300	- 60.741	- 10.000	.607
3700	13.718	71.256	60.534	39.669	- 60.782	- 8.589	.507
3800	13.764	71.622	60.821	41.043	- 60.822	- 7.177	.413
3900	13.808	71.980	61.103	42.422	- 60.865	- 5.766	.323
4000	13.850	72.331	61.379	43.805	- 60.910	- 4.353	.238
4100	13.890	72.673	61.651	45.192	- 60.957	- 2.938	.157
4200	13.927	73.008	61.917	46.583	- 61.006	- 1.522	.079
4300	13.963	73.336	62.179	47.977	- 61.056	- .105	.005
4400	13.997	73.658	62.436	49.375	- 61.109	1.311	- .065
4500	14.030	73.973	62.689	50.777	- 61.164	2.729	- .133
4600	14.061	74.281	62.938	52.181	- 61.220	4.154	- .197
4700	14.091	74.584	63.182	53.589	- 61.279	5.576	- .259
4800	14.120	74.881	63.423	55.000	- 61.339	6.998	- .319
4900	14.148	75.172	63.660	56.413	- 61.401	8.422	- .376
5000	14.174	75.459	63.893	57.829	- 61.465	9.844	- .430
5100	14.201	75.740	64.122	59.248	- 61.532	11.275	- .483
5200	14.226	76.016	64.348	60.669	- 61.600	12.700	- .534
5300	14.254	76.287	64.571	62.093	- 61.669	14.135	- .583
5400	14.279	76.553	64.791	63.520	- 61.741	15.560	- .630
5500	14.303	76.816	65.007	64.949	- 61.813	16.995	- .675
5600	14.328	77.074	65.220	66.381	- 61.889	18.426	- .719
5700	14.351	77.327	65.430	67.815	- 61.965	19.862	- .762
5800	14.375	77.577	65.637	69.251	- 62.043	21.299	- .803
5900	14.396	77.823	65.842	70.690	- 62.122	22.736	- .842
6000	14.422	78.065	66.044	72.131	- 62.203	24.174	- .880

March 31, 1961

WATER (H_2O) (IDEAL GAS) MOL. WT. = 18.016

ΔH_{f0}° = -57.103 kcal. mole^{-1} $\Delta H_{f\ 298.15}^\circ$ = -57.7979 kcal. mole^{-1}

Point Group C_{2v} $S^\circ_{298.15}$ = 45.106 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
3657.05 (1)
1594.59 (1)
3755.79 (1)

Bond Length and Angle O-H distance = 0.9584 Å H-O-H angle = 104.45° σ = 2

Product of Moments of Inertia $I_A I_B I_C$ = 5.7658 X 10^{-120} g.^{3} cm.^{6}

Heat of Formation

Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

Heat Capacity and Entropy

A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954), using the infra-red spectra analysis of W. S. Benedict, H. H. Claassen and J. H. Shaw, J. Research Natl. Bur. Standards 49, 91 (1952), have calculated the thermodynamic functions for water including the anharmonic corrections. Friedman and Haar in comparing their calculation to that of a direct summation by Glatt, Adams, and Johnston, Ohio State University Res. Foundation Tech. Report No. 316-8 (1953), found that the difference between the two calculations was less than the uncertainty in the direct summation.

C_p values from 100° to 5000°K. are from Friedman and Haar. C_p from 5000° to 6000°K was extrapolated linearly. Using the tabulated functions of Friedman and Haar C_p, S, and H_T-H_0 at T = 298.15°K. was calculated by the method of Lagrangian curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards 35, 151 (1945).

The bond length and angle were obtained from a compilation by L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chem. Soc., Burlington House, London W1, 1958.

Magnesium (Mg)

(Reference State) At. Wt. = 24.32

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 1.196	.000	.000	.000
100	3.768	2.273	12.695	- 1.042	.000	.000	.000
200	5.440	5.533	7.933	- .480	.000	.000	.000
298	5.973	7.814	7.814	.000	.000	.000	.000
300	5.980	7.851	7.814	.011	.000	.000	.000
400	6.290	9.613	8.052	.625	.000	.000	.000
500	6.560	11.047	8.512	1.267	.000	.000	.000
600	6.802	12.264	9.035	1.936	.000	.000	.000
700	7.080	13.333	9.577	2.629	.000	.000	.000
800	7.420	14.300	10.108	3.354	.000	.000	.000
900	7.810	15.196	10.624	4.115	.000	.000	.000
1000	7.880	18.339	11.304	7.034	.000	.000	.000
1100	8.140	19.102	11.979	7.836	.000	.000	.000
1200	8.400	19.821	12.602	9.563	.000	.000	.000
1300	8.660	20.504	13.184	9.516	.000	.000	.000
1400	4.968	43.187	14.072	40.760	.000	.000	.000
1500	4.968	43.530	16.025	41.257	.000	.000	.000
1600	4.968	43.850	17.754	41.754	.000	.000	.000
1700	4.968	44.152	19.298	42.251	.000	.000	.000
1800	4.968	44.436	20.687	42.748	.000	.000	.000
1900	4.968	44.704	21.944	43.244	.000	.000	.000
2000	4.969	44.959	23.088	43.741	.000	.000	.000
2100	4.969	45.201	24.136	44.238	.000	.000	.000
2200	4.970	45.433	25.098	44.735	.000	.000	.000
2300	4.972	45.654	25.987	45.232	.000	.000	.000
2400	4.974	45.865	26.811	45.729	.000	.000	.000
2500	4.978	46.068	27.578	46.227	.000	.000	.000
2600	4.983	46.264	28.292	46.725	.000	.000	.000
2700	4.989	46.452	28.962	47.224	.000	.000	.000
2800	4.998	46.633	29.589	47.723	.000	.000	.000
2900	5.009	46.809	30.180	48.223	.000	.000	.000
3000	5.023	46.979	30.737	48.725	.000	.000	.000
3100	5.040	47.144	31.264	49.228	.000	.000	.000
3200	5.060	47.304	31.763	49.733	.000	.000	.000
3300	5.085	47.460	32.235	50.240	.000	.000	.000
3400	5.114	47.613	32.686	50.750	.000	.000	.000
3500	5.148	47.761	33.115	51.263	.000	.000	.000
3600	5.186	47.907	33.524	51.780	.000	.000	.000
3700	5.229	48.050	33.914	52.301	.000	.000	.000
3800	5.278	48.190	34.288	52.826	.000	.000	.000
3900	5.332	48.327	34.646	53.356	.000	.000	.000
4000	5.392	48.463	34.990	53.892	.000	.000	.000
4100	5.457	48.597	35.320	54.435	.000	.000	.000
4200	5.528	48.729	35.638	54.984	.000	.000	.000
4300	5.604	48.860	35.944	55.541	.000	.000	.000
4400	5.686	48.990	36.239	56.105	.000	.000	.000
4500	5.773	49.119	36.524	56.678	.000	.000	.000
4600	5.866	49.247	36.799	57.260	.000	.000	.000
4700	5.964	49.374	37.065	57.851	.000	.000	.000
4800	6.067	49.501	37.323	58.453	.000	.000	.000
4900	6.176	49.627	37.573	59.065	.000	.000	.000
5000	6.289	49.753	37.815	59.688	.000	.000	.000
5100	6.407	49.878	38.050	60.323	.000	.000	.000
5200	6.530	50.004	38.279	60.970	.000	.000	.000
5300	6.658	50.130	38.501	61.629	.000	.000	.000
5400	6.790	50.255	38.718	62.301	.000	.000	.000
5500	6.927	50.381	38.929	62.987	.000	.000	.000
5600	7.069	50.507	39.135	63.687	.000	.000	.000
5700	7.215	50.634	39.335	64.401	.000	.000	.000
5800	7.367	50.760	39.531	65.130	.000	.000	.000
5900	7.523	50.888	39.722	65.875	.000	.000	.000
6000	7.684	51.015	39.910	66.635	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1962

MAGNESIUM (Mg) (REFERENCE STATE) AT. WT. = 24.32

Crystal	Below 922°K
Liquid	922°K to 1378°K
Ideal gas, monatomic	above 1378°K

See crystal, liquid, and ideal monatomic gas for details.