February 24, 1992

ANNUAL PERFORMANCE REPORT TO THE DEPARTMENT OF ENERGY

PROJECT DE-FG02-89ER-14080

DEVELOPMENT OF AN EXPERIMENTAL DATA BASE AND THEORIES FOR PREDICTION OF

THERMODYNAMIC PROPERTIES OF AQUEOUS ELECTROLYTES AND NONELECTROLYTES OF

GEOCHEMICAL SIGNIFICANCE AT SUPERCRITICAL TEMPERATURES AND PRESSURES

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Summary of Results

Research under this project is divided into three areas: experimental measurements, theoretical development, and geochemical applications. We have completed experimental volumetric measurements on aqueous solutions of CO_2, H_2S, CH_4, NH_3 and $B(OH)_3$ at 25 to 432°C and p – 280 and 350 bar. A new way of using our vibrating tube densitometer that allows density measurements near the bubble point and at the same time measures the bubble pressure was developed and used to measure densities and bubble pressures of aqueous CO_2. Heat capacity measurements on the same compounds should be completed by the end of the grant period.

On the theoretical side simulations of models for methane in water at temperatures to 1000° are in progress. In order to facilitate these free energy calculations the possible errors associated with the calculations have been explored in two papers (Wood, 1991; Wood et al., 1991) and methods of controlling and estimating these errors have been developed. The calculations on methane should be complete by the end of the grant period.

Experimental data collection is now well along and applications of the new data to geochemical processes is now possible. Meanwhile, efforts in this area have focussed on extracting equilibrium constants for carbonic acid dissociation at supercritical condition from published experiments on mineral equilibria in H_2O-CO_2 fluids (Böhlke and Shock, 1990; and in prep.). As a result, estimates of pKa for carbonic acid are now available at temperatures from 300° to 750°C and pressures from 1 to 7 kilobars. These estimates will be combined with the $\overline{V}°$ and $\overline{C}p°$ data for CO_2(aq) to improve the accuracy of thermodynamic data and mass-transfer calculations for geochemical reactions involving CO_2(aq).

INTRODUCTION

A detailed analysis of the processes that lead to the formation, migration, and accumulation of petroleum hydrocarbons is of vital economic and strategic importance. So too is the study of processes which govern the transport and deposition of metals and other inorganic species in sedimentary basins and in hydrothermal systems. Consideration of stable and metastable equilibria involving these aqueous species, minerals, gases, and condensed phases (solid and liquid) can lead to a more comprehensive understanding of a wide variety of geochemical processes, but requires accurate thermodynamic data for aqueous species at high pressures and temperatures. The long-term goals of this research are to create an experimental database and set of theoretical models which will allow accurate prediction of the thermodynamic properties of any aqueous solution component of significance to geochemical processes from normal surface conditions to the temperatures and pressures at which crustal rocks begin to melt. As a first step towards this goal we have measured volumes and are measuring heat capacities of aqueous solutions of H_2S, CO_2, CH_4, NH_3, and H_3BO_3, species of great geochemical significance. The second goal is to use this vastly expanded data base to both test existing theories and predictive methods and to develop new and highly refined theoretical approaches. As a result of our measurements the available high temperature calorimetric and volumetric data on aqueous nonelectrolytes will be roughly tripled. The free energies at any temperature and pressure are readily calculated from the well known values of enthalpies and free energies at 298.15 K and 1 bar, together with heat capacities and volumes at all T and P. Thus, the present measurements will yield more accurate values for free energies of these species from 25°C to ~430°C.

An undertaking of this type overlaps the field of physical chemistry and geochemistry. The success of this project depends upon the interdisciplinary combination of the expertise of three of us (RHW, LH, and CLL) in making these types of high temperature measurements and using physical chemical theories to model the results, together with the expertise of the other author (ELS) in developing geochemically applicable models for thermodynamic properties, fitting experimental data, and making extrapolations to higher temperatures and pressures, and finally applying the calculated thermodynamic properties to studies of the consequences of fluid/rock interactions.

EXPERIMENTAL MEASUREMENTS

Before starting measurements on these solutions, it was convenient to first find methods of storing and dispensing aqueous solutions of the solute in such a way that the concentration didn't change rapidly with time. The H_2S and CO_2 were stored in PVC pipes under a pressure of about 5 atm with the solutions being contained in an inner, aluminized mylar bag and expelled from the container by pumping water into the outer chamber of the vessel, thereby expelling the solution from inside the mylar bag. For methane, pressures of 100 bar are necessary, so we used a stainless steel bomb with a separator that moves up and down within the bomb to separate the aqueous methane solution from the driving fluid.

Heat capacity measurements are being measured with the flow, heat capacity apparatus developed previously (Biggerstaff et al., 1988; Carter and Wood, 1991). This apparatus measures the change in electric power necessary to keep the same temperature rise when switching from pure water to an aqueous solution in the flow stream. Recently this apparatus has been used to measure the heat

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capacities of aqueous electrolytes at pressures to 335 MPa and temperatures to and 425°C (Carter, 1992).

The densities have been measured with a vibrating tube densimeter described previously (Majer et al., 1991). Briefly, the densimeter measures the density of the aqueous solution relative to the density of pure water at the same temperature and pressure by measuring the period of a vibrating tube filled with the solution. The apparatus is calibrated using pure water and helium gas under pressure. The difference in density between pure water and a solution can be measured with an accuracy of about ±0.5% and with a sensitivity of about 10^{-4} g/cm^3.

RESULTS

The volumetric measurements on aqueous solutions of CH_4, CO_2, boric acid, ammonia, and H_2S at all temperatures and two or three pressures have been completed. Some preliminary measurements on aqueous carbon dioxide at high temperatures have been revised and published (Crovetto et al. 1991). The results of the other measurements are given in Table I and are in the process of being written up for publication. Some typical results of the volumetric measurements are given in Figures 1-2. The results show apparent molar volumes (which are roughly proportional to the compressibility of pure water) which peaks near 400°C at 28 MPa. This same behavior was observed in earlier measurements in this laboratory on argon, ethylene and xenon (Biggerstaff and Wood, 1988) and in exploratory measurements on CO_2 at high temperatures (Crovetto et al., 1990, 1991). This new volumetric data will allow reasonable extrapolation of the experimental solubilities of these gases at saturation pressure to high pressures. Solubilities of these gases have been measured up to about 350°C and the accuracy of the measurements is quite good up to 250°C, but the measurements get much more difficult and less accurate above this temperature. The heat capacity data will allow confirmation of these solubility results and calculation of the free energy of the aqueous species up to 425°C with pressures to 350 bar by integration of the heat capacity and volume results.

Most of the previous volumetric measurements on nonelectrolytes have been confined to temperatures below 100°C. Exceptions are (1) some previous measurements on argon, ethylene, and xenon from this laboratory, (2) boric acid, and (3) aqueous carbon dioxide at very high concentrations. The present results represent the first systematic exploration of the volumetric properties of aqueous nonelectrolytes at high temperatures. The importance of this kind of data is underscored by the failure of the best prediction schemes to accuratly predict these high temperature volumetric properties. For example, Figure 3 shows a comparison of measurements and predictions for $\bar{V}°$ of CO_2(aq) at 280 bar. It can be seen that the predictions of Shock et al. (1989) are considerably lower than the measured values. This type of discrepency is typical for the nonelectrolytes, and in the case of boric acid the predictions have the wrong sign. These kinds of failures are understandable because the authors had to rely on the room temperature data, a few high temperature equilibrium constants, and correlations based on previous measurements from this laboratory on argon, xenon and ethylene.

We have also used the vibrating tube densimeter to explore measurements on the bubble point of aqueous CO_2 solutions at high temperatures. This is a way of measuring the solubility of gases in water at high temperatures which is fairly easy and which gives accuracies that are not too bad near the critical

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point of water (approximately 10% in Henry's constant) (Crovetto and Wood, 1992). While making these measurements, the densities of the solutions close to the bubble point were obtained with 10 times greater accuracy than any previous measurements.

THEORETICAL MODELS

The recent increases in computing power now allow a whole new approach to the prediction of the properties of very high temperature aqueous solutions. Given a law of the forces between the atoms in the molecules of the solution, one can integrate Newton's laws of motion for these forces for say 300 molecules, allow them to equilibrate at any temperature desired, and by appropriate averaging of the properties calculate all of the thermodynamic properties for this model system. Of course the model compounds are not the real world, but the models for these species are becoming more and more accurate and by fitting the models to experimental data at lower temperatures, one can then extrapolate these models of the forces between atoms to estimate the properties of real solutions. The sensitivity of the predictions to the model parameters can also be assessed. The extrapolations have the advantage that the forces between atoms in the real world are independent of temperature.

We are primarily interested in the partial molar free energies of these gases at temperatures to 1000°C. The advantage of this kind of calculation is that it can be done at any temperature and pressure without any "experimental" problems. In a sense these are experimental results but in a model universe, that is, not the real universe.

One problem with these measurements is there have not been reliable ways to estimate the numerical accuracy with which free energies can be calculated by this procedure. Our first step in this project was to develop methods for estimating the systematic error due to the lag of the system configuration behind the Hamiltonian (Wood, 1991), and the systematic error due to the use of finite samples of configuration space in calculating the free energy (Wood et al., 1991).

Some preliminary results on equilibrium constant for methane solubility at high temperatures are given in Figure 4 which shows a contour plot of temperature vs. density on which the predicted equilibrium constants of Shock et al. (1989) are plotted against three experimental points with a Hamiltonian model simulation for methane. We are currently refining our Hamiltonian model so as to get the best possible estimates and then we'll do a grid of predictions at high temperatures and a variety of densities.

DISCUSSION

The volumetric measurements for aqueous nonelectrolytes described above permit revision of data and methods used to calculate thermodynamic properties of these species in fluid-driven geochemical processes. We are presently pursuing two approaches to these revisions. First, the revised Helgeson-Kirkham-Flowers (HKF) equations of state adopted by Shock et al. (1989) for aqueous nonelectrolytes are being used to regress the new data and obtain revised equation-of-state parameters. These parameters will allow improvements in the accuracy of predicted thermodynamic data calculated with the revised HKF equation throughout crustal conditions. Revised parameters will be presented in a format which will allow easy updating of the data files for the SUPCRT92 program

(Johnson et al., 1991) recently made available to the geochemical community. These revisions should help resolve some existing inconsistencies in nonelectrolyte properties as described below. Secondly, the new experimental data will be used to develop a new equation of state for geochemical calculations involving aqueous nonelectrolytes based on the density of H_2O rather than on its dielectric constant. Such an equation of state should be more intrinsically appealing as it will eliminate the need to evaluate effective Born coefficients which imply that formally neutral aqueous species have fractional charges. However, only if it retains and enhances predictive power will such an equation of state be as useful as the revised HKF equations for geochemical calculations. Therefore, considerable effort will go toward constructing correlations to estimate data for the multitude of nonelectrolytes (inorganic and organic) involved in geochemical processes for which experimental data may never be collected.

An example of the utility of the data already collected can be illustrated by considering aqueous CO_2. As shown in Figure 5 there is considerable divergence of calculated values of log K for carbonic acid dissociation (curves) and those determined experimentally (symbols) at pressures other than the vapor-liquid saturation pressures for H_2O (Psat). The curves in Figure 4 were calculated with equations, data and parameters from Shock et al. (1989). Part of the problem has been revealed by the lack of agreement between predicted values of $V_2^°$ for CO_2 and those measured as described above. Apparently, the magnitude of the effective Born coefficient obtained by Shock et al. (1989) by regression of CO_2 solubility data together with the Psat data in Figure 4 is too low. New regression results indicate that this coefficient could be as much as an order of magnitude greater. These results help to identify the problem, but the complete solution will require the heat capacity measurements currently underway.

Meanwhile, other lines of evidence confirm that the calculations shown in Figure 5 should be revised. Many metamorphic petrologists have conducted experiments to determine the effects of changing the mole fraction of CO_2 in CO_2-H_2O fluids on the stabilities of mineral assemblages. The data collected at the lowest mole fractions of CO_2, combined with thermodynamic data for minerals, H_2O and other aqueous species, allow retrieval of well-constrained estimates of log K for carbonic acid dissociation at supercritical conditions (Böhlke and Shock, 1990; and in prep.). These values of log K, which extend to temperatures above 600°C and pressures to 7 kb, connect smoothly with Read's data shown in Figure 5. Combined regression of these log K estimates with the volumetric and calorimetric data obtained in the present project will allow improved geochemical calculations with a new set of HKF parameters. As a result, it may be possible to reconcile differences in calculation methods and conceptual approaches to CO_2-H_2O fluids taken by aqueous geochemists and metamorphic petrologists. Applications of these results include studies of CO_2 speciation in fluid inclusions, generation of gold-quartz veins in the Mother Lode of California, albite/carbonate metasomatism by sodium bicarbonate fluids, and many other metamorphic-hydrothermal processes.

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TABLE I. ·   CH4   Mon, Feb 3, 1992 11:53 PM

	t/°C	P/MPa	molality	Δd	V-phi
1	25.00	28.00	0.140	-3.01	37.16
2	50.00	28.00	0.140	-2.98	37.50
3	100.00	28.00	0.140	-3.18	40.71
4	150.00	28.00	0.140	-3.49	46.01
5	200.20	28.00	0.140	-3.93	54.39
6	250.00	28.00	0.111	-3.46	65.50
7	300.00	28.00	0.137	-5.41	92.65
8	350.00	28.00	0.138	-7.86	167.55
9	379.90	28.00	0.138	-15.17	462.89
10	384.03	28.00	0.131	-16.93	608.54
11	387.19	28.00	0.132	-20.15	817.86
12	390.27	28.00	0.132	-24.35	1182.80
13	393.10	28.00	0.115	-23.00	1624.97
14	394.96	28.00	0.114	-20.59	1786.70
15	396.91	28.00	0.113	-16.33	1753.70
16	401.38	28.00	0.112	-8.05	1289.01
17	405.72	28.00	0.112	-4.66	980.88
18	412.32	28.00	0.112	-2.60	742.18
19	432.13	28.00	0.113	-0.92	475.56
20					
21					
22	25.00	35.00	0.140	-2.91	36.28
23	50.00	35.00	0.140	-2.95	37.11
24	100.00	35.00	0.140	-3.15	40.28
25	150.00	35.00	0.140	-3.50	45.85
26	200.00	35.00	0.140	-3.93	53.83
27	250.00	35.00	0.111	-3.42	64.13
28	300.00	35.00	0.137	-5.16	87.26
29	350.00	35.00	0.138	-6.62	136.14
30	395.08	35.00	0.114	-8.80	342.33
31	412.44	35.00	0.114	-10.48	681.73
32	421.83	35.00	0.113	-7.61	761.39
33	432.30	35.00	0.113	-4.06	630.66

	t/°C	P/MPa	molality	Δd	V-phi
1	25.00	1.00	0.155	1.65	34.37
2	25.00	20.00	0.155	1.61	33.43
3	50.00	20.00	0.155	1.58	33.84
4	100.00	20.00	0.155	1.11	37.80
5	150.00	20.00	0.155	0.63	42.69
6	200.20	20.00	0.155	0.01	50.05
7	250.00	20.00	0.185	-0.96	61.78
8	300.00	20.00	0.155	-2.05	84.62
9	350.00	28.00	0.155	-4.01	133.64
10	379.90	28.00	0.155	-10.48	349.37
11	384.03	28.00	0.157	-13.58	475.90
12	387.18	28.00	0.157	-16.80	643.68
13	390.26	28.00	0.157	-20.52	914.05
14	393.13	28.00	0.157	-22.45	1256.77
15	395.03	28.00	0.157	-20.42	1396.94
16	396.91	28.00	0.157	-16.37	1382.08
17	401.37	28.00	0.157	-7.90	1039.99
18	405.72	28.00	0.157	-4.36	811.16
19	412.31	28.00	0.157	-2.07	606.92
20	432.15	28.00	0.157	-0.40	409.20
21					
22					
23	25.00	28.00	0.195	1.82	33.37
24	25.00	35.00	0.155	1.57	33.54
25	50.00	35.00	0.155	1.58	33.70
26	100.00	35.00	0.155	1.16	37.25
27	150.00	35.00	0.155	0.70	41.86
28	200.20	35.00	0.155	0.14	48.42
29	250.00	35.00	0.185	-0.59	57.68
30	300.00	35.00	0.155	-1.42	74.14
31	350.00	35.00	0.155	-3.07	112.84
32	395.08	35.00	0.157	-7.63	283.72
33	412.47	35.00	0.157	-10.23	569.70
34	421.99	35.00	0.157	-7.09	623.42
35	432.23	35.00	0.157	-3.59	534.09

	t/°C	P/MPa	molality	Δd	V-phi
1	25.00	1.00	0.247	-0.15	34.78
2	25.00	20.00	0.247	-0.23	34.81
3	50.00	20.00	0.249	-0.44	35.99
4	100.00	20.00	0.251	-0.87	38.96
5	150.00	20.00	0.252	-1.35	43.02
6	200.20	20.00	0.254	-2.01	49.20
7	250.00	20.00	0.266	-2.89	58.26
8	300.00	20.00	0.260	-4.18	76.58
9	350.00	28.00	0.258	-6.19	113.69
10	379.90	28.00	0.257	-13.87	278.65
11	384.32	28.00	0.314	-22.15	395.08
12	387.18	28.00	0.235	-19.98	512.91
13	390.27	28.00	0.235	-24.58	736.17
14	394.96	28.00	0.235	-24.45	1119.81
15	401.40	28.00	0.235	-9.00	798.69
16	405.73	28.00	0.234	-4.91	618.65
17	412.34	28.00	0.234	-2.45	478.67
18	432.15	28.00	0.234	-0.57	337.98
19					
20					
21					
22	25.00	35.00	0.246	-0.34	35.03
23	50.00	35.00	0.249	-0.46	35.84
24	100.00	35.00	0.250	-0.81	38.43
25	150.00	35.00	0.252	-1.33	42.52
26	200.20	35.00	0.253	-1.83	47.67
27	250.00	35.00	0.267	-2.58	55.24
28	300.00	35.00	0.259	-3.37	67.90
29	350.00	35.00	0.259	-5.03	97.10
30	395.06	35.00	0.234	-8.70	218.17
31	412.42	35.00	0.234	-11.06	418.91
32	421.83	35.00	0.234	-7.90	467.98
33	432.38	35.00	0.234	-3.98	404.77

	t/°C	P/MPa	Δd, 0.2m	V-phi, 0.2m	Δd, 0.5m	V-phi, 0.5m	Δd, 0.75m	V-phi, 0.75m
1	25.00	0.10	4.36	39.77	10.72	40.04	15.81	40.22
2	25.00	28.00	4.28	39.95	10.57	40.11	15.67	40.18
3	25.00	10.00	4.32	39.81	10.63	40.06	15.83	40.03
4	100.00	10.00	3.83	43.25	9.41	43.51	14.03	43.45
5	140.68	10.50	3.67	44.93				
6	175.11	10.00	3.73	45.39	9.11	45.82	13.60	45.73
7	250.00	10.00	3.81	46.98	9.56	46.76	14.05	47.13
8	300.12	10.00	4.32	43.68	10.65	44.20	15.85	44.26
9	350.00	28.00	4.94	35.53	12.04	37.09	18.08	36.76
10	380.00	28.00	8.19	-35.38	19.85	-28.92	29.09	-24.96
11	383.97	28.00	9.69	-79.32	23.19	-67.26	33.69	-59.80
12	387.13	28.00	11.71	-146.73	27.78	-126.10	40.02	-112.80
13	390.22	28.00	14.75	-272.76	34.55	-232.83	49.34	-207.73
14	393.03	28.00	18.57	-493.76	43.39	-419.61	61.58	-371.79
15	395.10	28.00	19.85	-684.38	48.57	-609.84	70.68	-553.48
16	396.95	28.00	18.45	-782.35	47.29	-732.97	70.74	-682.97
17	401.57	28.00	11.45	-676.96	31.25	-699.61	49.68	-706.36
18	405.70	28.00	7.73	-524.10	20.67	-542.09	32.88	-560.60
19	412.26	28.00	5.07	-374.31	13.14	-378.62	20.44	-388.95
20	432.15	28.00	2.60	-168.56	6.50	-160.15	9.89	-163.79
21								
22								
23								
24								
25	25.00	37.00	4.30	39.78	10.61	39.96	15.78	39.96
26	100.00	35.00	3.87	42.78	9.52	43.01	14.01	43.22
27	175.12	35.00	3.71	45.15	9.14	45.37	13.60	45.35
28	250.00	35.00	3.76	46.81	9.23	47.20	13.83	47.01
29	300.15	35.00	3.99	46.38	9.80	46.89	14.55	46.99
30	350.00	35.00	4.55	40.82	11.30	41.13	16.74	41.50
31	395.28	35.00	7.25	-21.23	17.73	-16.74	26.21	-14.35
32	411.98	35.00	10.27	-178.13	25.10	-162.21	36.96	-151.72
33	421.95	35.00	9.33	-277.99	23.46	-265.46	35.42	-258.53
34	432.30	35.00	6.53	-259.01	16.69	-256.31	25.62	-258.42

	t/°C	P/MPa	molality	Δd	V-phi
1	25.01	20.00	0.197	-1.53	24.63
2	25.00	28.00	0.186	-1.44	24.49
3	100.00	10.00	0.197	-1.67	26.86
4	109.65	10.68	0.187	-1.53	26.81
5	120.50	10.63	0.187	-1.59	27.24
6	127.60	10.50	0.187	-1.60	27.77
7	129.90	10.50	0.187	-1.57	27.67
8	140.65	10.50	0.187	-1.62	28.35
9	175.12	10.00	0.197	-1.78	30.21
10	250.00	10.00	0.197	-2.06	37.30
11	300.15	10.00	0.197	-2.59	49.66
12	350.00	28.00	0.196	-2.91	63.56
13	379.90	28.00	0.196	-5.42	139.51
14	383.95	28.00	0.191	-5.98	171.50
15	387.12	28.00	0.191	-7.45	231.62
16	390.23	28.00	0.190	-9.11	326.75
17	393.00	28.00	0.190	-10.38	458.46
18	395.09	28.00	0.190	-9.84	539.90
19	396.95	28.00	0.190	-8.04	544.49
20	401.43	28.00	0.189	-4.04	429.49
21	405.70	28.00	0.189	-2.30	341.93
22	412.26	28.00	0.189	-1.28	280.88
23	432.08	28.00	0.188	-0.44	218.76
24					
25	25.00	37.00	0.197	-1.52	24.35
26	100.00	35.00	0.197	-1.67	26.45
27	175.13	35.00	0.197	-1.75	29.36
28	250.00	35.00	0.197	-1.99	35.23
29	300.12	35.00	0.197	-2.05	40.68
30	350.00	35.00	0.196	-2.62	56.83
31	395.28	35.00	0.187	-3.88	116.90
32	412.56	35.00	0.188	-4.95	226.08
33	422.03	35.00	0.188	-3.66	259.94
34	432.17	35.00	0.188	-2.09	240.29
35					
36					
37	25.00	0.10	0.398	-3.03	24.80
38	25.00	20.00	0.398	-3.18	24.91
39	25.00	28.00	0.366	-2.76	24.34
40	109.68	10.68	0.369	-3.09	27.05
41	350.00	28.00	0.394	-5.79	63.51
42	379.90	28.00	0.394	-10.80	140.12
43	383.95	28.00	0.379	-12.36	179.41
44	387.12	28.00	0.378	-15.02	238.89
45	390.23	28.00	0.378	-18.33	338.13
46	393.00	28.00	0.378	-20.64	475.32
47	395.09	28.00	0.377	-18.73	534.31
48	396.95	28.00	0.377	-15.35	539.16
49	401.43	28.00	0.376	-7.80	425.87
50	405.70	28.00	0.375	-4.60	347.19
51	412.26	28.00	0.375	-2.63	289.31
52	432.08	28.00	0.374	-0.96	229.96
53					
54	25.00	35.00	0.398	-3.14	24.57
55	395.28	35.00	0.372	-7.77	118.55
56	412.56	35.00	0.373	-9.78	227.84

	t/°C	P/MPa	molality	Δd	V-phi
57	422.03	35.00	0.373	-7.21	261.29
58	432.17	35.00	0.374	-4.10	239.80
59					
60					
61	25.00	0.10	0.810	-6.08	24.80
62	25.01	20.00	0.811	-6.34	24.82
63	99.99	10.00	0.811	-6.78	26.90
64	175.10	10.00	0.811	-7.30	30.38
65	250.00	10.00	0.811	-8.48	37.64
66	300.13	10.00	0.811	-10.81	50.66
67	350.00	28.00	0.800	-12.01	64.93
68	379.90	28.00	0.799	-22.86	100.82
69	383.96	28.00	0.779	-26.18	189.39
70	387.12	28.00	0.779	-32.35	258.11
71	390.24	28.00	0.778	-38.70	364.47
72	393.08	28.00	0.777	-41.07	490.98
73	395.05	28.00	0.776	-36.30	534.63
74	396.95	28.00	0.776	-28.86	522.52
75	401.45	28.00	0.773	-15.02	415.48
76	405.70	28.00	0.772	-9.05	342.54
77	412.27	28.00	0.772	-5.32	290.02
78	432.08	28.00	0.771	-2.04	235.11
79					
80	25.00	28.00	0.762	-5.89	24.60
81	25.00	37.00	0.811	-6.15	24.35
82	100.00	35.00	0.811	-6.75	26.45
83	175.12	35.00	0.811	-7.17	29.51
84	250.00	35.00	0.811	-7.78	34.77
85	300.13	35.00	0.811	-8.78	41.84
86	350.00	35.00	0.799	-10.66	57.48
87	395.28	35.00	0.768	-16.37	122.40
88	412.37	35.00	0.768	-19.77	228.96
89	422.07	35.00	0.769	-14.29	259.83
90	432.35	35.00	0.770	-8.16	239.18
91					
92					
93	25.00	0.10	1.564	-11.64	24.86
94	25.01	20.00	1.565	-11.81	24.68
95	99.99	10.00	1.565	-13.02	27.02
96	109.75	10.68	1.493	-12.40	27.25
97	175.10	10.00	1.565	-14.17	30.68
98	250.00	10.00	1.565	-16.30	37.94
99	300.16	10.00	1.565	-20.96	51.52
100	350.00	28.00	1.550	-23.42	66.39
101	380.00	28.00	1.549	-48.03	166.38
102	383.97	28.00	1.514	-56.03	219.09
103	387.14	28.00	1.514	-67.94	301.11
104	390.22	28.00	1.512	-76.57	411.71
105	393.08	28.00	1.511	-73.79	508.44
106	395.04	28.00	1.510	-61.80	519.82
107	396.95	28.00	1.510	-48.63	497.28
108	401.46	28.00	1.506	-26.23	400.26
109	405.71	28.00	1.504	-16.35	335.40
110	412.27	28.00	1.504	-9.85	287.29
111	432.28	28.00	1.504	-4.00	239.54
112					

	t/°C	P/MPa	molality	Δd	V-phi
113	25.00	28.00	1.494	-11.40	24.64
114	25.00	37.00	1.565	-12.26	24.74
115	100.00	35.00	1.565	-12.85	26.49
116	175.12	35.00	1.565	-13.75	29.66
117	250.02	35.00	1.565	-15.15	35.21
118	300.12	35.00	1.565	-17.05	42.41
119	350.00	35.00	1.549	-20.92	58.80
120	395.28	35.00	1.498	-32.16	127.16
121	412.46	35.00	1.500	-37.16	234.02
122	421.97	35.00	1.501	-26.30	257.71
123	432.24	35.00	1.502	-15.55	241.76
124					
125					
126	25.00	0.10	2.960	-21.61	24.80
127	25.01	20.00	2.962	-21.65	24.69
128	120.50	10.63	2.680	-21.64	27.58
129	127.60	10.50	2.680	-21.76	27.87
130	129.90	10.50	2.680	-21.83	27.98
131	140.70	10.50	2.680	-22.22	28.54
132	350.00	28.00	2.920	-43.29	35.26
133	379.90	28.00	2.920	-91.45	184.94
134	383.97	28.00	2.780	-105.35	252.64
135	387.14	28.00	2.780	-120.72	339.64
136	390.23	28.00	2.770	-124.40	431.93
137	393.03	28.00	2.770	-110.55	484.18
138	395.04	28.00	2.770	-90.06	475.11
139	396.94	28.00	2.760	-71.16	452.31
140	401.35	28.00	2.750	-40.23	369.49
141	405.72	28.00	2.740	-25.88	317.67
142	412.29	28.00	2.740	-15.81	273.46
143	432.18	28.00	2.730	-6.59	232.07
144					
145	25.00	28.00	3.106	-22.43	24.51
146	25.00	37.00	2.962	-21.99	24.58
147	350.00	35.00	2.920	-37.60	58.84
148	395.27	35.00	2.710	-58.60	135.44
149	412.52	35.00	2.720	-61.56	235.06
150	421.95	35.00	2.720	-42.57	250.71
151	432.50	35.00	2.730	-24.53	92.67

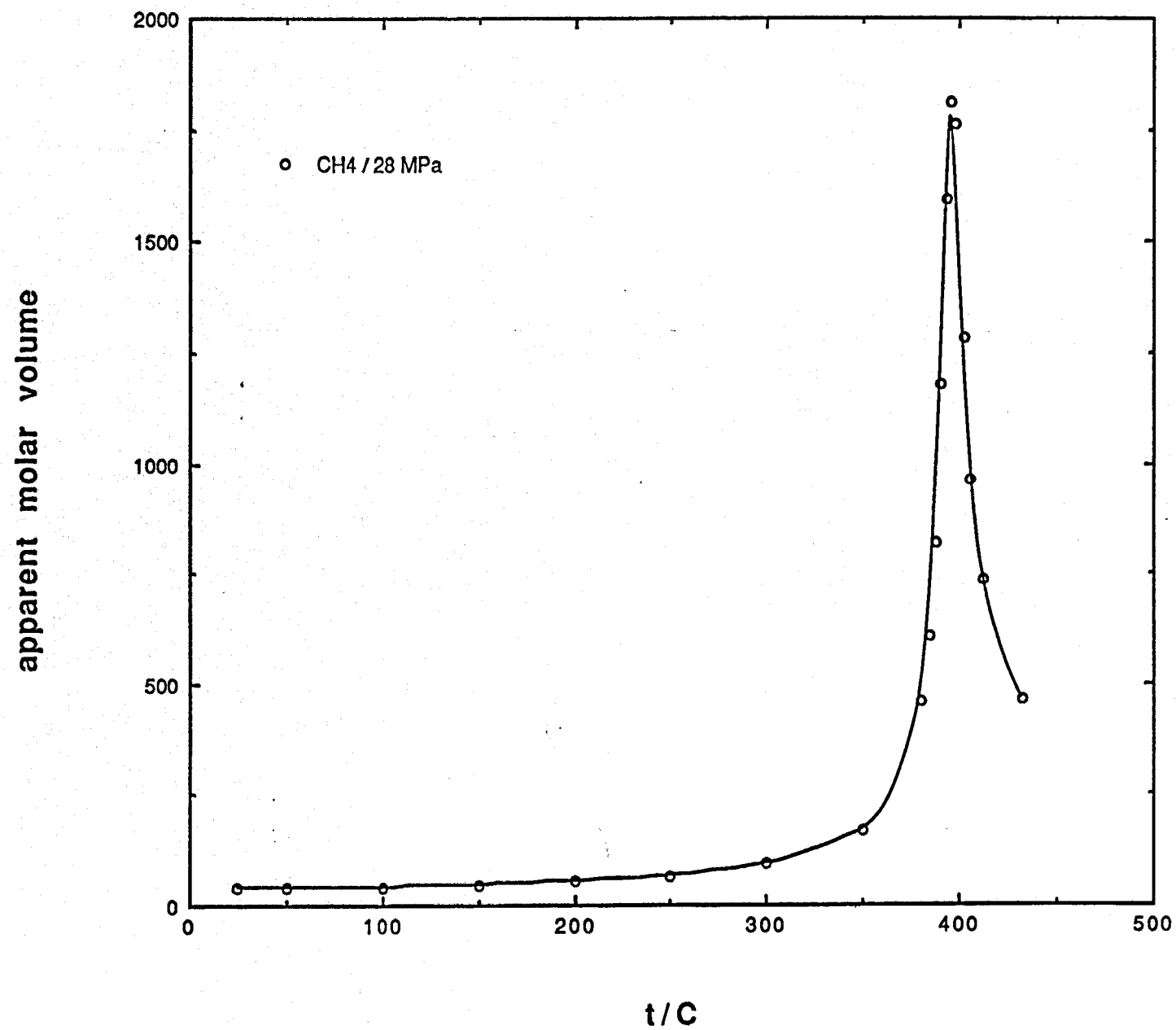|	t/°C	P/MPa	molality	Δd	V-phi

Figure 1. Apparent molar volume of CH_4(aq), 0.113 mol/kg) at 28 MPa vs. temperature.
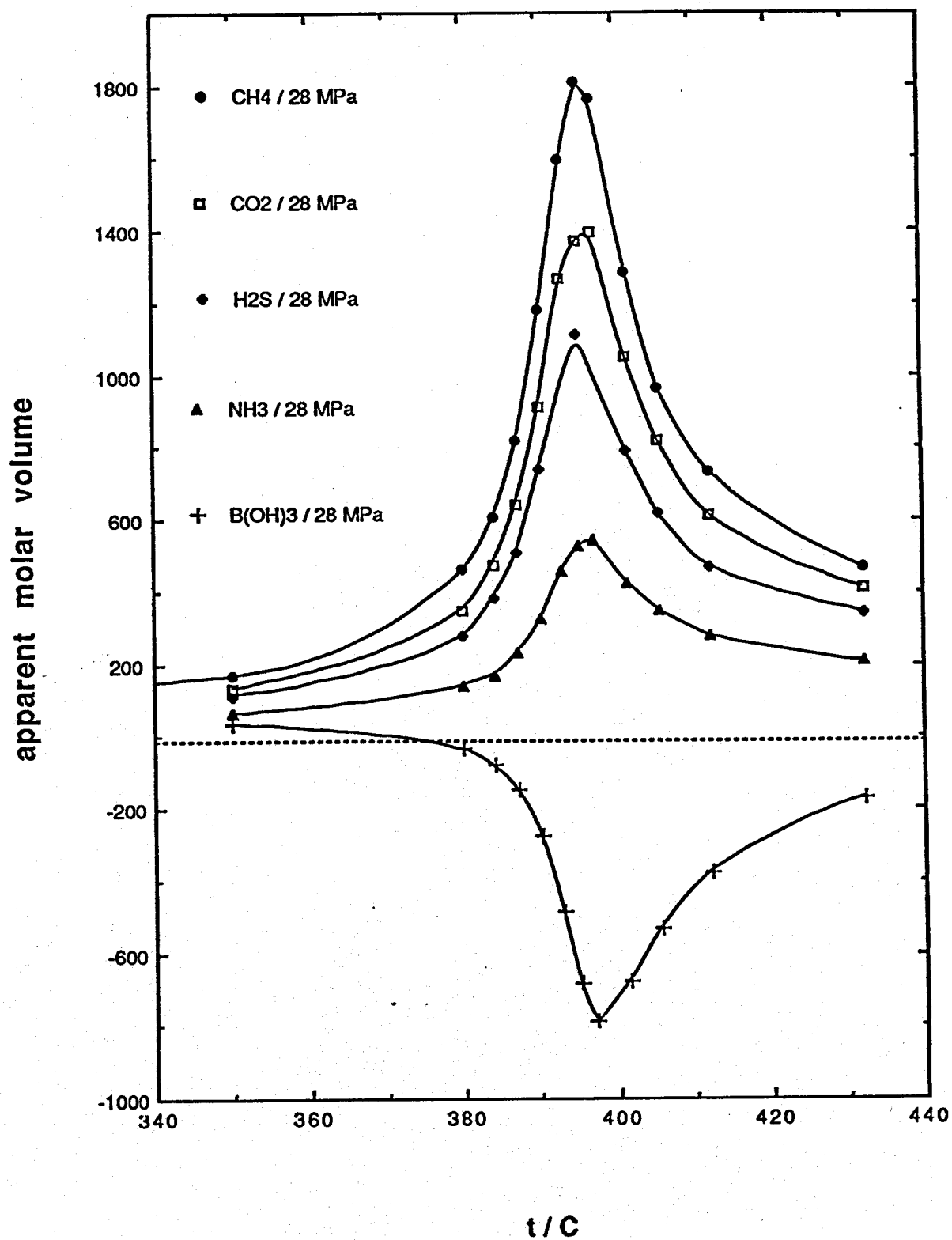
Figure 2. Apparent molar volume of CH_4 (aq, 0.113 mol/kg), CO_2 (aq, 0.115 mol/kg), H_2S (aq., 0.235 mol/kg), NH_3 (aq, 0.2 mol/kg), and $B(OH)_3$ (aq, 0.2 mol/kg) at 28 MPa vs. temperature.
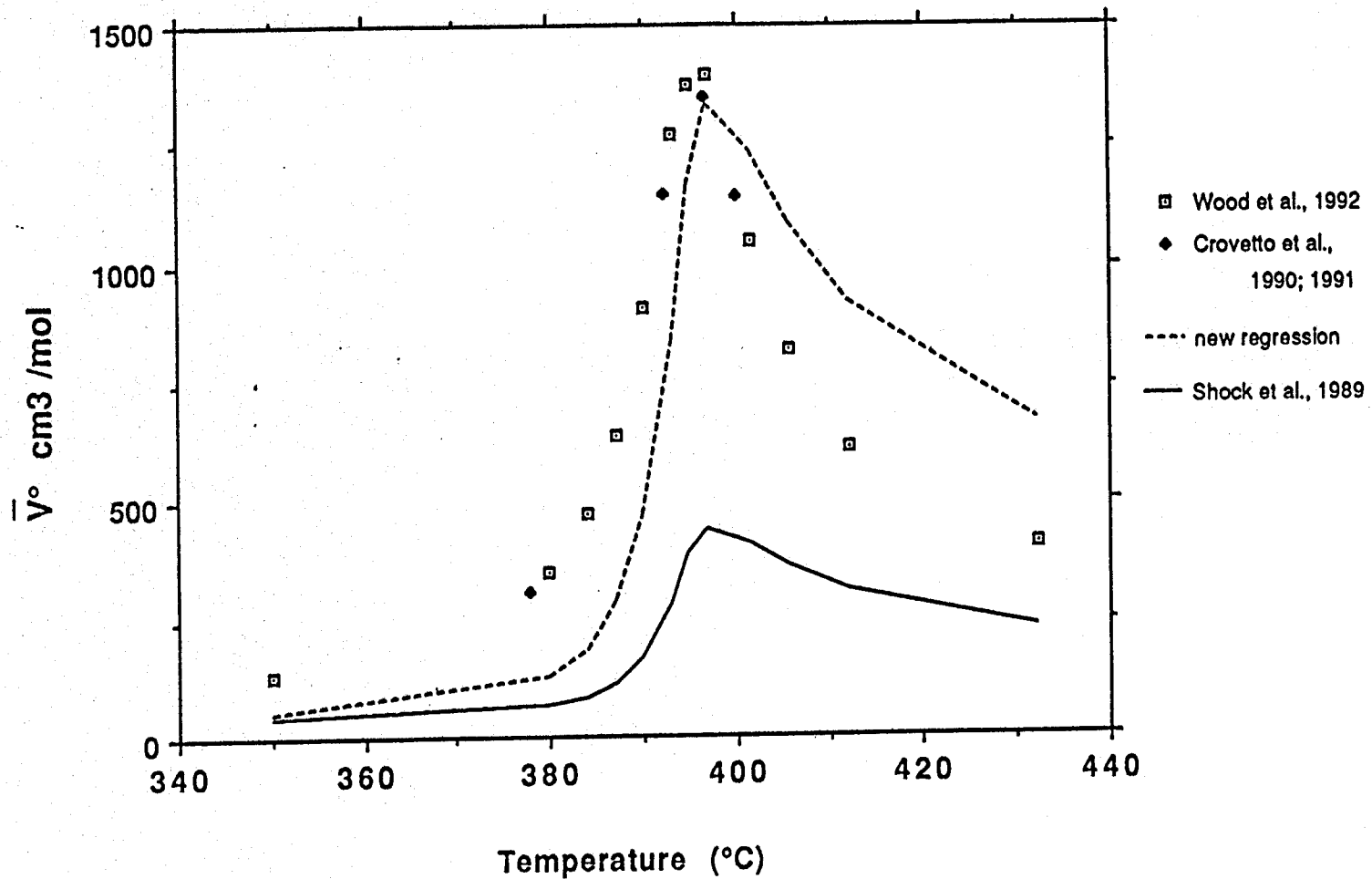
CO2 $\overline{V}°$ vs T   280 bars

Fig. 3. Plot of $\overline{V}°$ against temperature showing experimental values of $\overline{V}°$ for CO_2(aq) at 280 bars and predictions made with equations and parameters from Shock et al. (1989) (solid curve) and regression results with the revised-HKF equation of state (dashed curve) at the same pressure (see text).
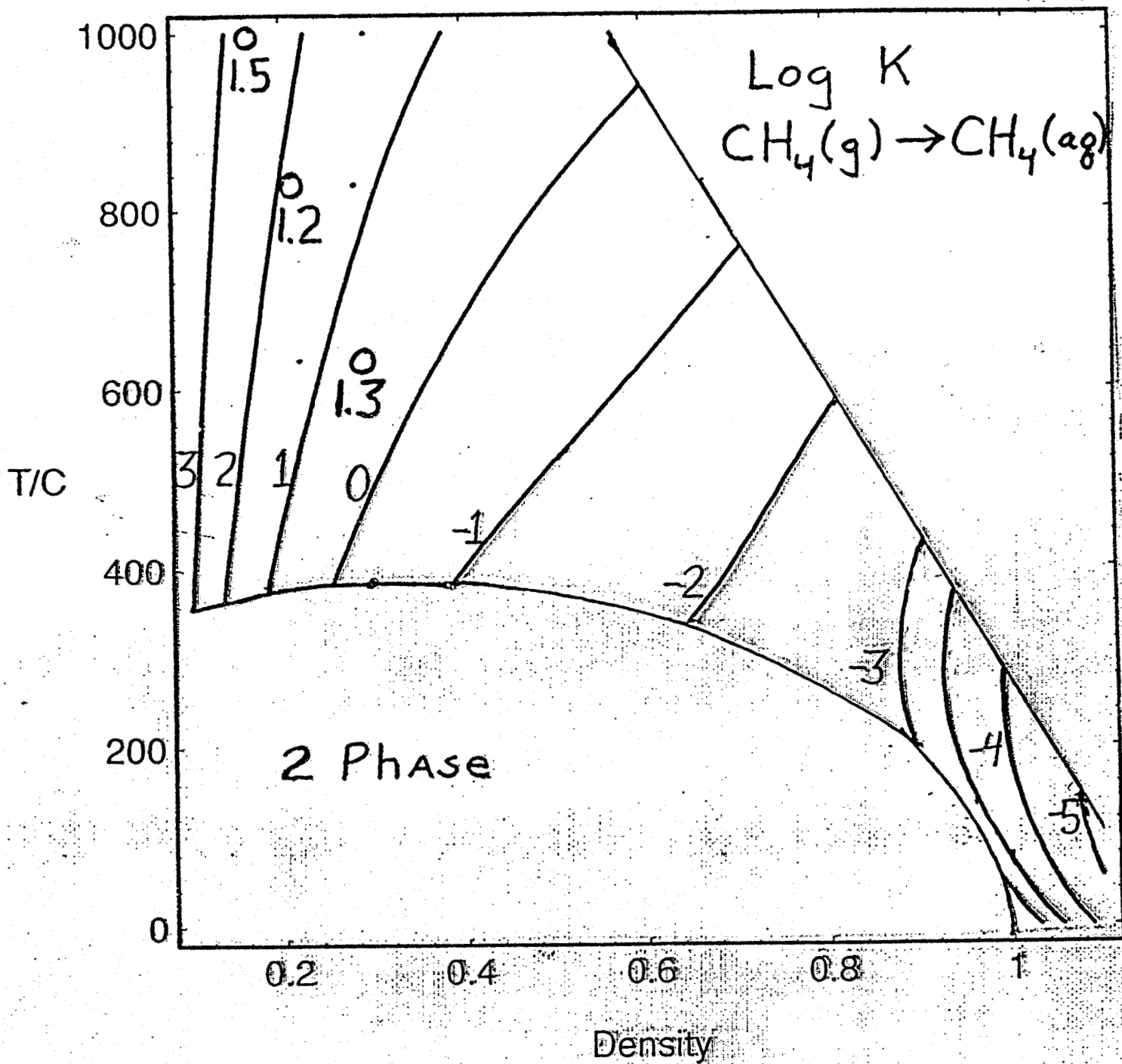
Fig. 4. Contour plot of Log K for $CH_4(g) \rightarrow CH_4(aq)$ vs. T and density of water. Points are results from preliminary simulations. Contour lines are the predictions of SUPCRT92 (Johnson et al., 1991) based on Shock and Helgeson (1990).
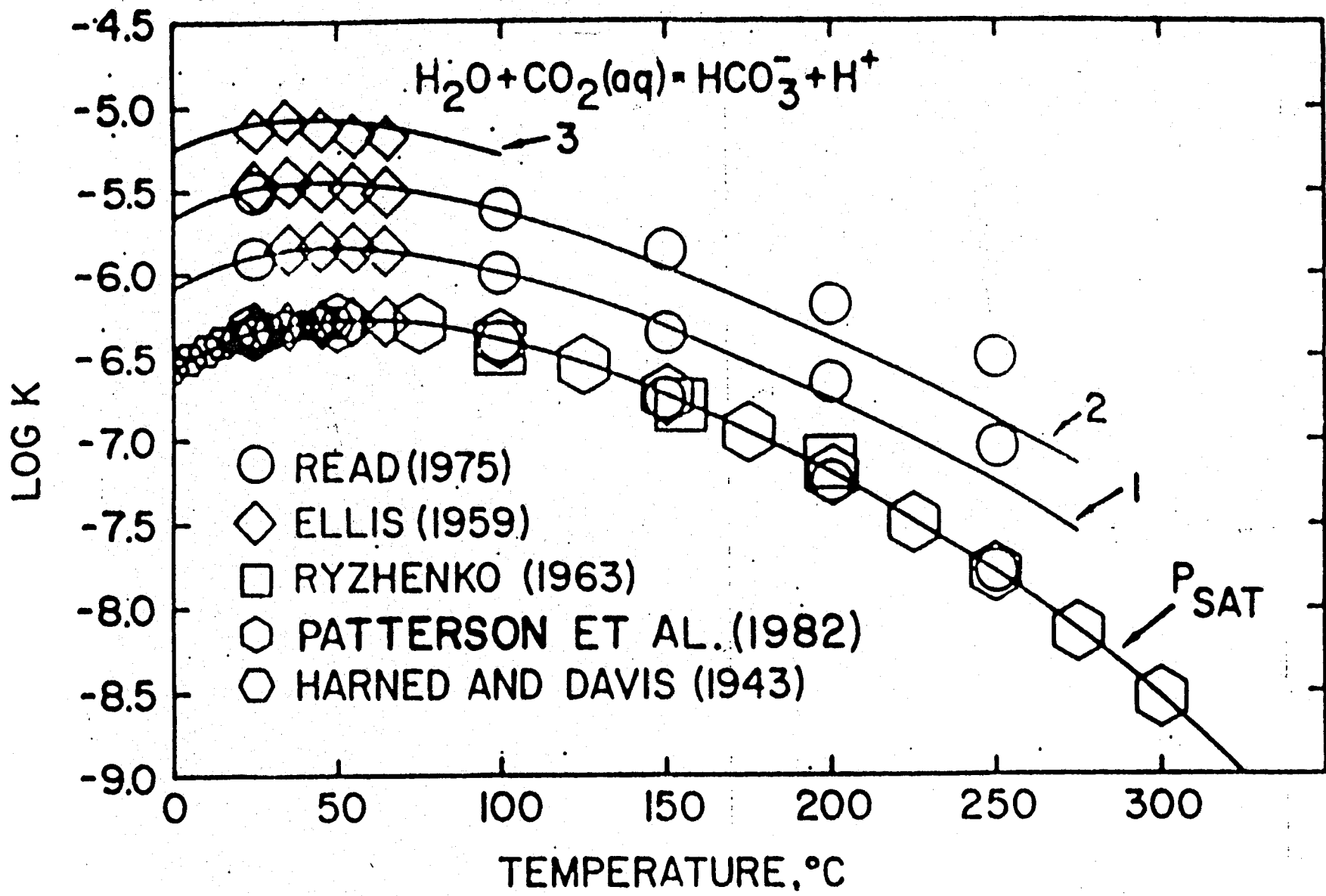
Figure 5. Log [K], the logarithm of the acid dissociation constant as a function of temperature and pressure. The lines are the predictions of Shock et al. (1989) at 3 kbar, 2 kbar, 1 kbar, and Psat.