Thiols in hydrothermal solution: Standard partial molal properties and their role in the organic geochemistry of hydrothermal environments

Mitchell D. Schulte[†,*] and Karyn L. Rogers[§]

[†] NASA Ames Research Center, Exobiology Branch, Mail Stop 239-4,
Moffett Field, CA 94035

[§] Washington University, Department of Earth & Planetary Sciences, Campus Box 1169,
One Brookings Drive, St. Louis, MO 63130

[*] Author to whom correspondence should be addressed (mschulte@mail.arc.nasa.gov)

Abstract - Modern seafloor hydrothermal systems are locations where great varieties of geochemistry occur due to the enormous disequilibrium between vent fluids and seawater. The disequilibrium geochemistry has been hypothesized to include reactions to synthesize organic compounds (Schulte and Shock, 1995; Shock and Schulte, 1998). Despite the incomplete understanding of the carbon budget in hydrothermal systems, the organic geochemistry of these sites has received little attention. Experimental simulations of these environments, however, indicate that organic compounds may have difficulty forming in a purely aqueous environment. On the other hand, thiols, thioesters and disulfides have been implicated as reaction intermediates between CO or CO_2 in experiments of carbon reduction in hydrothermal environments, as well as in a variety of biological processes and other abiotic reactions (Wächtershäuser, 1990; Heinen and Lauwers, 1996; Huber and Wächtershäuser, 1997; Russell et al., 1998). The reduction of CO_2 to thiols, for example, is observed using the FeS-H_2S/FeS_2 couple to provide the reducing power (see Schoonen et al., 1999). We have used recent advances in theoretical geochemistry to estimate the standard partial molal thermodynamic properties and parameters for the revised Helgeson-Kirkham-Flowers equation of state for aqueous straight-chain alkyl thiols. With these data and parameters we have evaluated the role that organic sulfur compounds may play as reaction intermediates during organic compound synthesis. We conclude that organic sulfur compounds may hold the key to the organic chemistry leading to the origin of life in hydrothermal settings. These results may also explain the presence of sulfur in a number of biomolecules present in ancient thermophilic microorganisms.

INTRODUCTION

Sulfur may play and may have played a key role in abiotic organic synthesis and biochemistry in hydrothermal environments (de Duve, 1991; Russell et al., 1998), and recent experimental work to model these environments appears to support this notion (Heinen and Lauwers, 1996; Huber and Wächtershäuser, 1997; Cody et al., 2000). Furthermore, the presence of sulfur in a number of key biological molecules (such as the amino acids cysteine, methionine and cystine, and coenzymes M and acetyl CoA) and metabolic processes (sulfur oxidation and reduction in a number of chemolithoautotrophs) also lends credence to this idea. The large number of oxidation states possible for sulfur makes for diverse chemistry, especially in combination with carbon. Thiols, the simplest sulfur-bearing organic compounds, are also common in biochemical processes and are, for example, responsible for the distinctive odors of garlic (2-propene-1-thiol), onions (propanethiol) and skunks (3-methyl-1-butanethiol).

Understanding the biochemical processes of the thermophilic microorganisms that inhabit hydrothermal environments and that can live to temperatures at least as high as 113°C (Blöchl et al., 1997) requires knowledge of the properties of the chemical reactions involved at elevated temperatures and pressures. In order to assess the role of aqueous organic sulfur compounds in hydrothermal organic geochemistry, we have been investigating their thermodynamic properties. We have culled the literature to obtain the experimentally determined properties of organic sulfur compounds. We were able to calculate a number of essential properties, such as free energies of formation, from solubility data available in the literature together with standard properties of organic sulfur gases. However, a number of the properties of aqueous organic sulfur compounds have not been experimentally determined. Furthermore, most of thermodynamic data that are available are only for 25°C and 1 bar. In order to determine reaction properties at the temperatures and pressures of the hydrothermal systems in which thermophilic organisms live, we use equations of state developed by Helgeson and co-workers (Helgeson et al., 1981); a summary of these equations is given in the Appendix. A key piece of information needed to extrapolate thermodynamic properties to elevated temperatures is the partial molal heat capacity, for which experimental data are unavailable for nearly all aqueous organic sulfur compounds, even at standard state conditions (25°C and 1 bar). We have used correlation methods to estimate the partial molal heat capacities and volumes of many organic solutes. These estimates allow us to asses the role of organic sulfur compounds during the reduction of carbon in hydrothermal settings.

ESTIMATION METHODS

Methods have been developed by Helgeson and co-workers (Schulte et al., 2001; Shock and Helgeson, 1988, 1990; Shock et al., 1989, 1992, 1997; Sverjensky et al., 1997) to estimate the standard partial molal thermodynamic properties of aqueous species. These methods have been extended to include aqueous organic compounds (Dale et al., 1997; Prapaipong et al., 1999; Schulte and Shock, 1993, 2001; Shock and Helgeson, 1990; Shock and Koretsky, 1993, 1995). Recent high temperature experimental measurements of the partial molal volumes and heat capacities of a selected group of compounds (Criss and Wood, 1996; Schulte et al., 1999) has led to improvements in these methods (Schulte, 1997; Schulte and Shock, 2001). Described below are the methods by which the standard partial molal thermodynamic properties of the aqueous alkyl thiols were calculated or estimated.

$\Delta\overline{G}_f^\circ$, $\Delta\overline{H}_f^\circ$ *and* $\overline{S}^\circ$

Values of the standard partial molal Gibbs free energy of formation $\left(\Delta\overline{G}_f^\circ\right)$ for aqueous methanethiol (CH_3SH) to butanethiol ($CH_3(CH_2)_3SH$) were calculated using the standard Gibbs free energy of formation of the gaseous species (Alberty et al., 1987) along with the Gibbs free energy of reaction for the hydration of the gas into the aqueous phase (Abraham et al., 1990). Similarly, the standard partial molal Gibbs free energy of formation for aqueous pentanethiol was calculated using data from Alberty et al. (1987) and Amoore and Buttery (1978). The standard partial molal enthalpies of formation $\left(\Delta\overline{H}_f^\circ\right)$ for aqueous methanethiol to butanethiol were calculated in a similar manner, using the standard enthalpies of formation of the gaseous species (Alberty et al., 1987) and enthalpies of hydration reactions (Abraham et al., 1990). Figures 1 and 2 show the resulting values of the standard Gibbs free energy of formation and standard enthalpy of formation, respectively, for the aqueous thiols as a function of the number of carbons in the alkyl chain (i.e. 1 for methanethiol (CH_3SH), 2 for ethanethiol (C_2H_5SH), etc.). As is evident in each figure, the standard partial molal thermodynamic properties of the alkyl thiols, like for all organic compound families, display systematic behavior as alkyl chain length increases. This behavior is due to the addition of the $-CH_2-$ group in increasing the chain length. The addition of this group increases the standard partial molal Gibbs free energy of formation of aqueous organic species by 2050 cal mol^{-1} and decreases the standard partial molal enthalpy by 5670 cal mol^{-1} (Shock and Helgeson, 1990). The straight lines shown on each plot represent best fit lines to the calculated data (shown as symbols in each plot) using 2050 cal mol^{-1} as the slope for the standard partial molal Gibbs free energy of formation and -5670 cal mol^{-1} for the standard partial molal enthalpy of formation. The best line fits to the calculated data using these slopes results in intercepts of the lines of -4370 cal mol^{-1} for $\Delta\overline{G}_f^\circ$ and -6180 cal mol^{-1} for $\Delta\overline{H}_f^\circ$, allowing us to calculate these properties for straight-chained aqueous thiols for which experimental data are not available. The equations used to make these estimates are

$$\Delta\overline{G}_f^\circ = -4370 + 2050\overline{n} \tag{1}$$

and

$$\Delta\overline{H}_f^\circ = -6180 + 5670\overline{n} , \tag{2}$$

where $\overline{n}$ represents the number of carbons in the alkyl chain.

Values of the standard partial molal entropy $(\overline{S}^\circ)$ of aqueous methanethiol to butanethiol were calculated using the values of $\Delta\overline{G}_f^\circ$ and $\Delta\overline{H}_f^\circ$, along with values of S° of the elements from Cox et al. (1989). Figure 3 shows the resulting values of the standard partial molal entropy as a function of the number of carbons in the alkyl chain, along with a best fit line to these values using the slope of 6.7 cal mol^{-1} K^{-1} taken from Shock and Helgeson (1990) for aqueous organic species. The line corresponds to the equation

$$\overline{S}^\circ = -33.1 + 6.7\overline{n}, \tag{3}$$

allowing us to calculate $\overline{S}^\circ$ for aqueous thiols for which calculation of the entropy from the free energy and enthalpy, as described above, cannot be made. The values of $\overline{S}^\circ$ for methanethiol to butanethiol, obtained as described above, are listed in Table 1.

$\overline{C}_P^\circ$ *and* $\overline{V}^\circ$

Because there are no experimental data for the standard partial molal volumes and heat capacities of aqueous thiols, even at the standard conditions of 25°C and 1 bar, we have estimated these properties for the aqueous thiols. In order to estimate the heat capacities, we compared the standard partial molal heat capacity of the aqueous amino acid serine to that of the aqueous amino acid cysteine. These two amino acids are identical in structure, except for the functional group at the terminal end of the alkyl chain[1]. In serine, the terminal functional group is a hydroxyl (-OH). In cysteine, the terminal functional group is a thiol (–SH). The experimentally determined value of the standard partial molal heat capacity of serine is 28.1 cal mol^{-1} K^{-1} (Jolicoeur and Boileau, 1978), while the standard partial molal heat capacity of cysteine is 44.9 cal mol^{-1} K^{-1} (Jolicoeur et al., 1986). Therefore, the difference in the standard partial molal heat capacity of these two aqueous molecules is 16.8 cal mol^{-1} K^{-1}. This value is, then, the difference in standard partial molal heat capacity between a molecule containing a thiol group relative to that containing a hydroxyl group. Because the amino acids that were compared each contain three carbons in their alkyl chains, we have chosen to add the difference in standard partial molal heat capacity, 16.8 cal

---

[1] The structure of serine is $HO\text{-}CH_2\text{-}(CH)NH_2\text{-}COOH$, while that of cysteine is $HS\text{-}CH_2\text{-}(CH)NH_2\text{-}COOH$. Note that the difference in the structures is the left-hand terminal functional group (-OH in serine and -SH in cysteine).

mol^{-1} K^{-1}, to that of propanol to estimate the heat capacity of propanethiol[2]. The resulting value of the standard partial molal heat capacity of aqueous propanethiol is 101.1 cal mol^{-1} K^{-1}. Values of $\overline{C}_P^\circ$ for the other aqueous thiols at 25°C and 1 bar were then estimated by adding or subtracting multiples of 21.2 cal mol^{-1} K^{-1} from this value, following the arguments of Shock and Helgeson (1990) on the systematic behavior of partial molal heat capacities of aqueous organic compound families.

Values of the standard partial molal volume for the aqueous alkyl thiols were estimated in a manner similar to that used for the heat capacities. The difference in standard partial molal volumes between serine ($\overline{V}^\circ$ = 60.57 cm^3 mol^{-1}; Cabani et al., 1981) and cysteine ($\overline{V}^\circ$ = 73.44 cm^3 mol^{-1}; Millero et al., 1978) is 12.87 cm^3 mol^{-1}. This value was added to the partial molal volume of propanol to estimate the partial molal volume of propanethiol, resulting in a value of 83.57 cm^3 mol^{-1}. The partial molal volumes of aqueous organic compounds also vary systematically wtih carbon number (Shock and Helgeson, 1990), and multiples of 15.8 cm^3 mol^{-1} were added or subtracted from this value as a function of carbon number to estimate the standard partial molal volumes of other aqueous thiols at 25°C and 1 bar.

To gain an appreciation of how accurate the estimated values may be, we have plotted the $\overline{C}_P^\circ$ and $\overline{V}^\circ$ of the aqueous thiols against the number of carbons in the alkyl chain in Figure 4. We have added to the plot the experimentally determined values for aqueous H_2S (which plots at $\overline{n}$ = 0). The values of $\overline{C}_P^\circ$ and $\overline{V}^\circ$ we would estimate by the methods described above for $\overline{n}$ = 0 are 37.5 cal K^{-1} mol^{-1} and 37.17 cm^3 mol^{-1}, respectively, while the experimental values for H_2S are 42.7 cal K^{-1} mol^{-1} and 34.92 cm^3 mol^{-1}, respectively. Our estimated values are consistent with the experimental values for hydrogen sulfide, giving us confidence in our estimation methods.

Helgeson-Kirkham-Flowers equation of state parameters

---

[2] The structure of propanol is HO-CH_2-CH_2-CH_3, while that of propanethiol is HS-CH_2-CH_2-CH_3. The difference in these two compounds is the presence of a hydroxyl as the terminal functional group in propanol, and the presence of a thiol as the terminal functional group in propanethiol.

The standard state thermodynamic properties estimated for aqueous alky lthiols at 25°C and 1 bar listed in Table 2 were used to obtain parameters for the revised Helgeson-Kirkham-Flowers (HKF) equations of state (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock et al., 1992) using correlation algorithms for aqueous nonelectrolytes (including neutral organic species) presented by Shock and Helgeson (1990), Schulte et al. (2001) and Schulte and Shock (2001). The resulting parameters are also listed in Table 2. These data and parameters were used with the revised HKF equations of state (see appendix) to calculate standard state properties at elevated temperatures and pressures. Such calculations are facilitated by using the SUPCRT92 computer program (Johnson et al., 1992), which is available free of charge from Prof. Harold Helgeson at the University of California, Berkeley.

FORMATION OF AQUEOUS THIOLS IN HYDROTHERMAL ENVIRONMENTS

Surface promoted catalysis on sulfide minerals may lead to the formation of thiols in hydrothermal environments (see e.g. Huber and Wächtershäuser, 1997; Russell et al., 1998; Cody et al., 2000). The following reactions describe the formation of aqueous methanethiol from CO (Equation (4)), CO_2 (Equation (5)), H_2S and H_2, the most likely starting materials for organic synthesis in hydrothermal environments, especially on the early Earth:

$$CO(aq) + H_2S(aq) + 2\,H_2(aq) = \underset{\text{methanethiol}}{CH_3SH(aq)} + H_2O \tag{4}$$

$$CO_2(aq) + H_2S(aq) + 3\,H_2(aq) = \underset{\text{methanethiol}}{CH_3SH(aq)} + 2\,H_2O\ . \tag{5}$$

The carbon in CO or CO_2 is reduced by the hydrogen and hydrogen sulfide that is produced by reactions among sulfur-bearing minerals (e.g. pyrite and pyrrhotite). Longer chain thiols can be formed similarly, according to the general reaction shown on Figure 5. Figure 5 depicts the logarithms of the equilibrium constants of the reactions for thiol formation from CO for methanethiol (C_1) to decanethiol (C_{10}) as a function of temperature at saturation pressure. Figure 6 shows these for thiol formation from CO_2. These plots indicate that the formation of thiols from simple starting materials is energetically favored at temperatures commonly encountered in hydrothermal environments. In addition, it is evident from comparing the curves in Figures 5 and 6 that reactions that form thiols from CO are more thermodynamically favorable (log K is more positive) than the corresponding reactions starting with CO_2, and is favorable to higher temperatures (~300°C for formation from CO vs. ~200°C for formation from CO_2). This result is consistent with arguments put forward by Schoonen et al. (1999) in which the role of electron orbitals in carbon reduction reactions is discussed, and indicates that perhaps CO is the more likely source of reduced carbon in hydrothermal environments. Figure 5 also indicates that formation of longer chained compounds is more thermodynamically favorable than those of the shorter chained compounds to a temperature of about 300°C. Similar conclusions were reached by Shock and Schulte (1998) in their study of the potential for organic synthesis during fluid mixing in hydrothermal systems. Based on these results, we have calculated the potential for production of the simplest thiol, methanethiol, in modern and early Earth hydrothermal systems, taking into account the geochemical constraints imposed by modern and early Earth hydrothermal environments.

Modern Systems

Geochemical constraints consist of naturally buffered activities and fugacities of the chemical species that participate in these reactions. Measurements of the aqueous hydrogen concentrations of vent fluids are consistent with the pyrite-pyrrhotite-magnetite (PPM) mineral assemblage (Shock et al., 1995). Therefore, model calculations for modern hyrothermal systems assume activities of H_2 and H_2S in equilibrium with the PPM mineral assemblage (see Table 3). For the formation of methanethiol from CO, the activity of CO in modern hydrothermal systems is assumed to be a relatively conservative value of 10^{-6} ($\log a_{CO} = -6$). For calculations involving CO_2, the activity of CO_2 is set to 13.8 mM, taken from a compilation of measured CO_2 concentrations for modern seafloor hydrothermal vent systems (Von Damm, 1990). For the following model calculations, the activity of H_2O is assumed to be unity (Helgeson et al., 1993) and we have assumed a total pressure of 250 bars, consistent with a 2.5 km deep seafloor hydrothermal system.

The final geochemical constraint we place on our model calculations is the equilibrium constant for the reaction. We use the relation

$$\log K = \frac{\Delta \overline{G}_r^{\circ}}{-2.303RT} \tag{6}$$

to obtain values of the logarithm of the equilibrium constant (K) at appropriate temperatures and pressures, where $\Delta \overline{G}_r^{\circ}$ is the standard Gibbs free energy of the reaction at elevated temperature and pressure, R is the gas constant and T is the temperature in Kelvin. For each reaction the law of mass action is used to determine the equilibrium activity of methanethiol. For example, at equilibrium

$$K_4 = \frac{\left(a_{CH_3SH}\right)\left(a_{H_2O}\right)}{\left(a_{CO}\right)\left(a_{H_2S}\right)\left(a_{H_2}\right)^2} \tag{7}$$

where K_4 stands for the equilibrium constant of reaction (4) above and a_i refers to the activity of each chemical species (*i*) involved in the reaction, raised to the stoichiometric reaction coefficient (which is positive for products and negative for reactants). Taking the logarithm and rearranging the law of mass action of reaction (4) gives

$$\log a_{CH_3SH} = \log K_4 + \log a_{CO} + \log a_{H_2S} + 2 \log a_{H_2}, \quad (8)$$

which allows us to assess the activity of aqueous methanethiol given the geochemical constraints discussed above. Similarly, we have also calculated the equilibrium methanethiol activities for formation by CO_2, as illustrated by Equation (5). The corresponding law of mass action reduces to

$$\log a_{CH_3SH} = \log K_5 + \log a_{CO_2} + \log a_{H_2S} + 3 \log a_{H_2}. \quad (9)$$

The logarithm of the aqueous methanethiol activity can be calculated using Equation (9) and the geochemical constraints discussed above.

The potential for methanethiol formation from CO and CO_2 can be calculated as a function of temperature using Equations (8) and (9) and values of the geochemical constraints adjusted for temperature. The resulting values of the logarithm of the equilibrium methanethiol activity from reactions (4) and (5) are shown as a function of temperature in Figure 7. Examination of Figure 7 reveals that if methanethiol forms from CO, its activity can be as high as 0.1 (at lower temperatures), while formation of methanethiol from CO_2 gives an activity as high as 10^{-5}. Note that the calculated equilibrium activities of methanethiol are much greater from forming by reduction of CO than CO_2 by 4 orders of magnitude. The highest calculated activities are at the lowest temperatures, and kinetic barriers may prevent the formation reactions from proceeding under these conditions. In addition, the calculated activities assume that the CO or CO_2 is *only* converted into methanethiol, and does not consider the formation of other carbon compounds or consumption of CO and CO_2 in the system. Therefore it is unlikely that these high concentrations would be reached. On the other hand, the catalytic activity of the sulfide minerals abundant in these systems may help overcome these barriers and significant amounts of thiols may indeed form and accumulate in these environments.

Archean Systems

Hydrothermal systems were likely to be present on the early Earth, and may have been more prevalent than in the modern day. Furthermore, the rocks controlling the composition of the vent fluids may have been more reducing than modern mid-ocean ridge basalts (MORBs). This would result in more hydrogen production during alteration of the crust, and the potential for even greater organic synthesis (Schulte and Shock, 1995). Therefore, we have performed calculations similar to those above using a set of geochemical constraints appropriate for Archean hydrothermal systems. We assume that the hydrogen activity in ancient hydrothermal systems was buffered by the FMQ (fayalite-quartz-magnetite) mineral assemblage (see Table 3). Since the FMQ mineral buffer does not itself contain any sulfur-bearing minerals, we must couple the FMQ buffer to the pyrrhotite-magnetite (PM) mineral assemblage to constrain the aqueous H_2S activity. We use the activity of aqueous H_2 required by FMQ equilibrium as a function of temperature from 0-350°C to determine the aqueous H_2S activity in equilibrium with the pyrrhotite-magnetite reaction (see Table 3) as a function of temperature. The values of CO and CO_2 activity are assumed to be consistent with models of increased amounts of these gases in the Archean atmosphere. It has been postulated that the partial pressures of CO and CO_2 were as high as 1 and 10 bars, respectively, on the early Earth (Kasting, 1993). We have adopted these values for simplification for our calculations of the methanethiol activity in Archean hydrothermal systems. Using the geochemical constraints of Archean hydrothermal systems described above, along with Equations (8) and (9), we can calculate the equilibrium methanethiol activities as a function of temperature. The results are shown in Figure 8. Because of the greater reduction potential in the early Earth systems, the calculated equilibrium activity of methanethiol is much higher than in the case of modern systems. Formation of methanethiol from CO gives activities as high as 10^3, while formation from CO_2 gives activities as high as 10^{-1}. Again, low temperatures may prevent these reactions from reaching equilibrium; however, methanethiol activities at higher temperature are still significant. The potential is much greater to form organic compounds from CO than from CO_2.

THIOLS AS REACTION INTERMEDIATES IN MODERN AND EARLY EARTH HYDROTHERMAL SYSTEMS

Recent experimental and theoretical evidence indicates that thiols may be necessary intermediates for the formation of aqueous organic molecules, such as carboxylic acids, amino acids, hydrocarbons and alcohols, in hydrothermal environments (Heinen and Lauwers, 1996; Huber and Wächtershäuser, 1997; Russell et al., 1998; Schoonen et al., 1999; Cody et al., 2000). The formation of these molecules may involve the attachment of precursors (such as CO, CO_2 or formaldehyde) to sulfide mineral surfaces, followed by the reduction of the attached molecule to thiols, then formation of carboxylic acids, alcohols, or amino acids from the intermediate thiols.

In order to assess the role of aqueous thiols as intermediate species, we have calculated the equilibrium constants of some reactions involving simple aqueous thiols, alcohols and carboxylic acids in hydrothermal environments. The reactions forming methanol from methanethiol and ethanol and acetic acid from ethanethiol are shown in Table 4. The equilibrium constants for these reactions are plotted as a function of temperature at 250 bars in Figure 9. Note that in each case the formation of the products is favored at all temperatures relevant to hydrothermal systems. This indicates that once formed, thiols would react to produce other organic species. If we now take into account the same geochemical constraints discussed above for thiol formation, we can calculate the amount of organic species that would form in hydrothermal systems from the previously calculated activities of thiols.

As shown previously, the equilibrium thiol activity depends on the geochemical constraints imposed by the system and the carbon source for thiol formation (e.g. CO or CO_2). In order to assess the production of methanol from methanethiol in modern and early Earth hydrothermal systems, we used the equilibrium methanethiol activities calculated previously and shown in Figures 7 and 8, along with geochemical constraints imposed by the environment. In addition, we calculated equilibrium activities of ethanethiol for formation from CO and CO_2 in order to assess the production of ethanol and acetic acid from ethanethiol. The results for both modern and early Earth hydrothermal systems, with the formation of the intermediate thiol from both CO and CO_2, are shown in Figure 10. In general, equilibrium activities of alcohols and carboxylic acids are quite high, especially at low temperatures. At temperatures relevant to hydrothermal systems, production of these simple organic compounds from alkyl thiols is quite significant. By comparing figures 10A and 10C with 10B and 10D, respectively, we find that the higher equilibrium activities of thiols formed from CO rather CO_2 have resulted in higher activities of alcohols and carboxylic acids. By comparing Figure 10A to 10C and 10B to 10D, we can begin to understand how geochemical constraints can control organic compound production in hydrothermal systems. Higher activities of methanol, ethanol and acetic acid can be expected in Archean hydrothermal systems than in modern examples because of the different amounts of thiol, H_2 and H_2S available in each system. Furthermore, in modern hydrothermal systems, methanol takes over as the most abundant organic compound of the three at very high temperatures, while in early Earth systems acetic acid is most abundant over the entire temperature range. Of course, these calculations provide upper limits on the production of these compounds, as they do not take into account the formation of other organic compounds and the competition among all organic compounds for the carbon available in the system.

Experimental Analogs

While thiols have not been measured previously from hydrothermal systems, some experimental work may indicate that they could be intermediate species in such environments. Seewald (1994) demonstrated experimentally that predicted metastable equilbrium states do exist among organic species (aqueous hydrocarbons) under hydrothermal conditions. Because Seewald (1994) used sulfide-bearing minerals to control the oxidation state in his experiments, we believe that thiols were likely to have formed during his experiments and here we calculate the concentrations that should have been achieved based on his results. At 350 bars pressure and

325°C, the reported concentration of H_2S (aq) was 6.1×10^{-3} molal and the H_2(aq) concentration was 0.36×10^{-3} molal, consistent with buffering by the pyrite-pyrrhotite-magnetite mineral assemblage used in the experiments. The ethane concentration was reported to be 1.6×10^{-3}. From the logarithm of the equilibrium constant for the reaction

$$C_2H_6(aq) + H_2S(aq) = C_2H_5SH(aq) + H_2(aq), \quad (11)$$

ethane ethanethiol

along with the reported concentrations of ethane, H_2S and H_2, we calculate that ethanethiol should have reached a concentration of 1.9×10^{-6} molal, or approximately 2 ppm. Such a concentration should be detectable and would provide a direct test of these estimated data, as well as the achievement of metastable equilibrium among organic sulfur and other organic species. Similarly, any other hydrothermal experiments conducted using sulfide minerals as redox buffers have the potential to generate thiols that may be present in metastable equililbrium concentrations.

CONCLUDING REMARKS

Using previously developed methods, as well as some new correlations and techniques, we have estimated standard partial molal thermodynamic properties of aqueous alkyl thiols. These estimates also allow calculation of reaction properties involving aqueous thiols at elevated temperatures and pressures using the revised HKF equations of state. We are now capable of incorporating these compounds into geochemical models of hydrothermal organic geochemical systems.

The results shown here imply that aqueous thiols may play a key role in the organic geochemistry of hydrothermal systems. In general, the formation of longer chain thiols from CO or CO_2, H_2S and H_2 is more favorable than the formation of shorter chain thiols at temperatures below 250°C. This result lends support to previous models of organic acid formation in hydrothermal systems that conclude that the longer chain acids are more favorable to form at lower temperatures (Shock and Schulte, 1998). In addition, the formation of these compounds from carbon monoxide is more facile that formation from carbon dioxide. For example, the activity of methanethiol can theoretically reach values as high as 0.1 and 10^{-5} from CO and CO_2, respectively, in modern hydrothermal environments (see Figure 7). Extrapolating to the early Earth, the calculated values of methanethiol activities rise to as much as 1000 (from CO) and 10^{-2} (from CO_2). These high activities of methanethiol would result in a concomitant increase in the potential for production of organic compounds for which thiols serve as reaction intermediates.

The formation of alcohols and carboxylic acids from thiols is thermodynamically favored, indicating that thiols may serve as reaction intermediates between CO or CO_2 and other organic compounds. The formation of organic compounds from thiols would create a positive feedback, in which the consumption of thiols during organic compound synthesis would drop the thiol activity below equilibrium values, thus driving further thiol synthesis and allowing thiols to persist in hydrothermal environments. We would encourage researchers making measurements of fluid samples from these systems to include these and other kinds of organic sulfur compounds in their analyses.

While the formation of thiols from either CO or CO_2 is favored at temperatures and pressures relevant in hydrothermal systems, the amount of thiols that may be produced in these environments depends on the geochemical constraints imposed by each system. Thus, not only is the carbon source a major factor in determining the equilibrium thiol activity, but the composition of the inorganic components of the system plays a role in the distribution of organic compounds as well. For example, over a range of temperatures relevant to hydrothermal systems, the production of methanethiol from CO in an early Earth system is much greater than that in a modern system (see Figures 7 and 8). The importance of these geochemical constraints is evident when exploring the formation of alcohols and carboxylic acids using thiols as reaction intermediates. For example, in Archean hydrothermal systems, acetic acid is always more abundant than ethanol or methanol, whereas in modern systems, methanol is the most abundant of these three above 300°C. In modern systems, the activity ratio of methanethiol to acetic acid is 1 at approximately 250°C, and the reaction to form acetic acid is thermodynamically favored. In early Earth systems, the higer values of thiol activity would result in a concomitant increase in the potential for production of organic compounds for which thiols serve as reaction intermediates.

The elevated potential of thiol synthesis in early Earth hydrothermal systems places thiols in a key role of organic compound synthesis. The presence of sulfur in many essential biomolecules, including coenzyme-M, which is itself a thiol, supports this notion. Organic compound synthesis from thiols may have led to the first 'geochemical metabolic cycles' from which modern metabolism is derived. If life started in a hydrothermal environment, organic reactions may have taken place on sulfur-bearing mineral surfaces, which acted not only as catalysts, but also as a source for the sulfur that drove the first primitive metabolic cycles.

Acknowledgments - This work was funded in part by the National Research Council and the Exobiology Branch at NASA Ames Research Center (MDS). KLR was supported by an NSF Graduate Research Fellowship and a Stanford Graduate Fellowship while at Stanford University, and is currently supported by a Mr. and Mrs. Spencer T. Olin Fellowship for Women in Graduate Study at Washington University. We would like to thank the RIDGE program for providing funding to help defray the costs of attending and for organizing the 5th RIDGE Theoretical Institute on the Subsurface Biosphere at Mid-Ocean Ridges, where this work was first presented. We would like to thank Tom McCollom, Everett Shock, Jan Amend, Mike Russell, Sherwood Chang and Hal Helgeson for encouragement and many helpful discussions.

REFERENCES

Abraham M. H., Whiting G. S., Fuchs R. and Chambers E. J. (1990) Thermodynamics of solute transfer from water to hexadecane. *J. Chem. Soc. Perkins Trans.* **2** 1990, 291-300

Alberty R. A., Burmenko E., Kang T. H. and Chung M. B. (1987) Standard chemical thermodynamic properties of alkanethiol isomer groups. *J. Phys. Chem. Ref. Data* **16**, 193-208.

Amoore J. E. and Buttery R. G. (1978) Partition coefficients and comparative olfactometry. *Chem. Senses and Flavour* **3**, 57-71.

Blöchl E., Rachel R., Burggraf S., Hafenbradl D., Jannasch H. W and Stetter K. O. (1997) *Pyrolobus fumarii*, gen. and sp. nov., represents a novel group of archaea, extending the upper temperature limit for life to 113°C. *Extremophiles* **1**, 14-21.

Cabani S., Gianni P., Mollica V. and Lepori L. (1981) Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J. Solution Chem.* **10**, 563-595.

Cody G. D., Boctor N. Z., Filley T. R., Hazen R. M., Scott J. H., Sharma A., Yoder, Jr. H. S. (2000) Primordial carbonylated iron-sulfur compounds and the synthesis of pyruvate. *Science* **289**, 1337-1340.

Cox J. D., Wagman D. D., and Medvedev V. A. (eds.) (1989) *CODATA Key Values for Thermodynamics*, Hemisphere Pub. Corp, New York.

Criss C. M. and Wood R. H. (1996) Apparent molar volumes of aqueous solutions of some organic solutes at the pressure 28 MPa and temperatures to 598K. *J. Chem. Thermodynam.* **28**, 723-741.

Dale J. D., Shock E. L., MacLeod G., Aplin A. C. and Larter S. R. (1997) Standard partial molal properties of aqueous alkylphenols at high pressures and temperatures. *Geochim. Cosmochim. Acta* **61**, 4017-4024.

de Duve C. (1991) *Blueprint for a Cell: The Nature and Origin of Life*. Neil Patterson Publishers, Carolina Biological Supply Company.

Heinen W. and Lauwers A. M. (1996) Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment. *Orig. Life Evol. Biosphere* **26**, 131-150.

Helgeson H. C., Kirkham D. H. and Flowers G. C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. *Amer J. Sci.* **281**, 1249-1516.

Helgeson H. C., Knox A. M., Owens C. E. and Shock E. L. (1993) Petroleum, oil field brines and authigenic mineral assemblages: Are they in metastable equilibrium? *Geochim. Cosmochim. Acta* **57**, 3295-3340.

Huber C. and Wächtershäuser G. (1997) Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. *Science* **276**, 245-247.

Johnson J. W., Oelkers E. H. and Helgeson H. C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Comput.Geosci.* **18**, 899-947.

Jolicoeur C. and Boileau J. (1978) Apparent molal volumes and heat capacities of low molecular weight peptides in water at 25°C. *Can. J. Chem.* **56**, 2707-2713.

Jolicoeur C., Reidl B., Desrochers D., Lemelin L. L., Zamojska R. and Enea O. (1986) Solvation of amino acid residues in water and urea-water mixtures: Volumes and heat capacities of 20 amino acids in water and in 8 molar urea at 25°C. *J. Solution Chem.* **15**, 109-128.

Kasting J. F. (1993) Earth's early atmosphere. *Science* **259**, 920-926.

Millero F. J., Lo Surdo A. and Shin C. (1978) The apparent molal volumes and adiabatic compressibilities of aqueous amino acids at 25°C. *J. Phys. Chem.* **82**, 784-792.

Prapaipong P., Shock E. L. and Koretsky C. M. (1999) Metal-organic complexes in geochemical processes: Temperature dependence of the standard thermodynamic properties of aqueous complexes between metal cations and dicarboxylate ligands. *Geochim. Cosmochim. Acta* **63**, 2547-2577.

Russell M. J., Daia D. E. and Hall A. J. (1998) The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean. In *Thermophiles: The keys to molecular evolution and the origin of life?* (J. Wiegel and M. W. W. Adams eds.) Taylor & Francis, London.

Schoonen M. A. A., Xu Y. and Bebie J. (1999) Energetics and kinetics of the prebiotic synthesis of simple organic acids and amino acids with the FeS-H_2S/FeS_2 redox couple as reductant. *Orig. Life Evol. Biosphere* **29**, 5-32.

Schulte M. D. (1997) Synthesis and processing of aqueous organic compounds during water/rock reactions. Ph.D. Thesis, Washington University, St. Louis, MO.

Schulte M. D. and Shock E. L. (1993) Aldehydes in hydrothermal solution: Standard partial molal thermodynamic properties and relative stabilities at high temperatures and pressures. *Geochim. Cosmochim. Acta* **57**, 3835-3846.

Schulte M. D. and Shock E. L. (1995) Thermodynamics of Strecker synthesis in hydrothermal systems. *Orig. Life Evol. Biosphere* **25**, 161-173.

Schulte M. D. and Shock E. L. (2001) Organic compounds in hydrothermal solutions, in prep.

Schulte M. D., Shock E. L., Obsil M. and Majer V. (1999) Volumes of aqueous alcohols, ethers, and ketones to $T = 523$ K and $p = 28$ MPa. *J. Chem. Thermodynam.* **31**, 1195-1229.

Schulte M. D., Shock E. L. and Wood R. H. (2001) The temperature dependence of the standard state thermodynamic properties of aqueous nonelectrolytes. *Geochim. Cosmochim. Acta*, in press.

Seewald J. S. (1994) Evidence for metastable equilibrium between hydrocarbons under hydrothermal conditions. *Nature* **370**, 285-287.

Shock E. L. (1995) Organic acids in hydrothermal solutions: Standard molal thermodynamic properties of carboxylic acids and estimates of dissociation constants at high temperatures and pressures. *Amer. J. Sci.* **295**, 496-580.

Shock E. L. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. *Geochim. Cosmochim. Acta* **52**, 2009-2036.

Shock E. L. and Helgeson H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* **54**, 915-945.

Shock E. L. and Koretsky C. M. (1993) Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. *Geochim. Cosmochim. Acta* **57**, 4899-4922.

Shock E. L. and Koretsky C. M. (1995) Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. *Geochim. Cosmochim. Acta* **59**, 1497-1532.

Shock E. L. and Schulte M. D. (1998) Organic synthesis during fluid mixing in hydrothermal systems. *J. Geophys. Res.* **103**, 28513-28527.

Shock E. L., Helgeson H. C. and Sverjensky D. A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* **53**, 2157-2183.

Shock E. L., McCollom T. and Schulte M. D. (1995) Geochemical constraints on chemolitho-autotrophic reactions in hydrothermal systems. *Orig. Life Evol. Biosphere* **25**, 141-159.

Shock E. L., Oelkers E. H., Johnson J. W., Sverjensky D. A. and Helgeson H. C. (1992) Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000°C and 5 kbar. *J. Chem. Soc. Faraday Trans.* **88**, 803-826.

Shock E. L., Sassani D. C., Willis M. and Sverjensky D. A. (1997) Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* **61**, 907-950.

Stull D. R., Westrum, Jr. E. F., and Sinke G. C. (1969) *The Chemical Thermodynamics of Organic Compounds*. J. Wiley & Sons, New York.

Sverjensky D. A., Shock E. L. and Helgeson H. C. (1997) Prediction of the thermodynamic properties of aqueous complexes to 1000°C and 5 kb. *Geochim. Cosmochim. Acta* **61**, 1359-1412.

Tanger J. C. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. *Amer. J. Sci.* **288**, 19-98.

Von Damm K. L. (1990) Seafloor hydrothermal activity: Black smoker chemistry and chimneys. *Ann. Rev. Earth Planet. Sci.* **18**, 173-204

Wächtershäuser G. (1990) The case for the chemoautotrophic origin of life in an iron-sulfur world. *Orig. Life Evol. Biosphere* **20**, 173-176.

APPENDIX

Standard State Conventions

The standard state employed in this study for gases is unit fugacity of the hypothetical ideal gas at any temperature and 1 bar. The standard state convention for aqueous species adopted in the present study is one of unit activity in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. The standard state for H_2O calls for unit activity of the pure solvent at any pressure and temperature.

Summary of the Revised HKF Equations of State

One approach to calculating standard state properties for aqueous organic acids at high pressures and temperatures which allows estimates and predictions for many species involves the revised Helgeson-Kirkham-Flowers (HKF) equations of state (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock et al., 1992). Data and parameters for several groups of organic compounds are given by Shock and Helgeson (1990), Schulte (1997), Schulte and Shock (1993; 2001) and Dale et al. (1997). The data and parameters for monocarboxylic acids have been updated and extended, and combined with data and parameters for dicarboxylic acids, hydroxy acids, benzoic acid and toluic acids by Shock (1995). The latter set of data and parameters for organic acids were used in the thermodynamic calculations described in the text.

The standard partial molal properties of aqueous species are expressed in the revised HKF equations of state in terms of structural and solvation contributions. A general statement of this summation for any standard partial molal property of the *jth* aqueous species, Ξ_j°, can be expressed by

$$\Xi_j^\circ = \Delta\Xi_n^\circ + \Delta\Xi_s^\circ \tag{A–1}$$

where the subscripts n and s refer to the nonsolvation (or structural) and solvation contributions, respectively. The revised HKF equations for the standard partial molal volume, $\overline{V}^{\circ}$, and heat capacity, $\overline{C}_P^{\circ}$, are given by (Tanger and Helgeson, 1988)

$$\overline{V}^{\circ} = \Delta\overline{V}_n^{\circ} + \Delta\overline{V}_s^{\circ}$$

$$= \sigma + \frac{\xi}{T - \theta} - \omega Q + \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T$$

$$= a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P}\right)\left(\frac{1}{T - \theta}\right) - \omega Q + \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T , \tag{A–2}$$

and

$$\overline{C}_P^{\circ} = \Delta\overline{C}_{P,n}^{\circ} + \Delta\overline{C}_{P,s}^{\circ}$$

$$= c_1 + \frac{c_2}{(T - \theta)^2} - \left(\frac{2T}{(T - \theta)^3}\right)\left(a_3(P - P_r) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right)$$

$$+ \omega T X + 2 T Y\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P , \tag{A–3}$$

where ξ, σ, a_1, a_2, a_3, a_4, c_1, c_2 and ω represent species-dependent equation of state parameters, Ψ and θ designate solvent-dependent parameters equal to 2600 bars and 228 K for H_2O, T and P stand for temperature and pressure, P_r signifies the reference pressure of 1 bar, and Q, Y, and X indicate the Born functions defined by

$$Q \equiv \frac{1}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial P}\right)_T , \tag{A–4}$$

$$Y \equiv \frac{1}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P , \tag{A–5}$$

and

$$X \equiv \left(\frac{\partial Y}{\partial T}\right)_P = \frac{1}{\varepsilon}\left[\left(\frac{\partial^2 \ln \varepsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P^2\right], \tag{A–6}$$

where ε stands for the dielectric constant of H_2O. Equations (A-2) and (A-3) have been used to regress experimental data for aqueous inorganic and organic electrolytes at elevated temperatures and pressures (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; 1990; Shock, 1995; Shock and Koretsky, 1993, 1995; Shock et al., 1997; Sverjensky et al., 1997; Prapaipong et al., 1999), and are consistent with the approach of $\overline{V}^\circ$ and $\overline{C}_P^\circ$ of aqueous electrolytes to $-\infty$ at the critical point of H_2O (373.917°C and 220.46 bars).

In the case of neutral aqueous species, the solvation terms in the revised HKF equations of state can be expressed in terms of the effective Born coefficient (ω_e), which is given for the *nth* neutral species by (Shock et al., 1989)

$$\omega_{e,n} = \frac{\eta Z_{e,n}^2}{r_{e,n}} \qquad \text{(A–7)}$$

where $r_{e,n}$ and $Z_{e,n}$ refer to the effective electrostatic radius and effective charge of the *nth* neutral aqueous species, respectively, and $\eta = 1.66027 \times 10^5$ (Å cal mol^{-1}). Regression of experimental data is consistent with the assumption that the effective Born coefficients of neutral aqueous species are independent of temperature and pressure (Shock et al., 1989; 1992; Shock and Helgeson, 1990; Sverjensky et al., 1997; Shock, 1995; Schulte and Shock, 2001; Schulte et al., 2001). It follows that the revised HKF expressions for the solvation contributions to the standard partial molal volumes and heat capacities of neutral aqueous species are given by

$$\Delta\overline{V}_s^\circ = -\omega_e Q \qquad \text{(A–8)}$$

and

$$\Delta\overline{C}_{P,s}^\circ = \omega_e T X . \qquad \text{(A–9)}$$

As a consequence, the revised HKF expressions for the standard partial molal volume and heat capacity of neutral aqueous species correspond to (Shock et al., 1989)

$$\overline{V}^\circ = a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P}\right)\left(\frac{1}{T - \theta}\right) - \omega_e Q \qquad \text{(A–10)}$$

and

$$\overline{C}_P^\circ = c_1 + \frac{c_2}{(T - \theta)^2} - \left(\frac{2T}{(T - \theta)^3}\right)\left(a_3(P - P_r) + a_4\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right) + \omega_e T X . \tag{A-11}$$

Integration of Eqn. (A-11) with respect to temperature yields

$$\overline{S}^\circ = \overline{S}^\circ_{P_r,T_r} + c_1\ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\theta}\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{T_r - \theta}\right) + \frac{1}{\theta}\ln\left(\frac{T_r(T - \theta)}{T(T_r - \theta)}\right)\right]$$

$$+ \left(\frac{1}{T - \theta}\right)^2\left(a_3(P - P_r) + a_4\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right) + \omega_e\left(Y - Y_{P_r,T_r}\right) , \tag{A-12}$$

where T_r indicates the reference temperature of 298.15 K.

The apparent standard partial molal Gibbs free energy and enthalpy of formation are given by (Benson, 1976; Helgeson et al., 1981; Tanger and Helgeson, 1988)

$$\Delta\overline{G}^\circ \equiv \Delta\overline{G}_f^\circ + \left(\overline{G}^\circ_{P,T} - \overline{G}^\circ_{P_r,T_r}\right) \tag{A-13}$$

and

$$\Delta\overline{H}^\circ \equiv \Delta\overline{H}_f^\circ + \left(\overline{H}^\circ_{P,T} - \overline{H}^\circ_{P_r,T_r}\right) \tag{A-14}$$

where $\Delta\overline{G}_f^\circ$ and $\Delta\overline{H}_f^\circ$ stand for the conventional standard partial molal Gibbs free energy and enthalpy of formation at the reference conditions of 1 bar and 298.15 K, respectively, and the parenthetical terms represent the difference between the standard partial molal Gibbs free energy and enthalpy of formation at the reference conditions and those at the temperature and pressure of interest. It follows from Eqns. (A-2), (A-3), (A-13), and (A-14) together with

$$\overline{H}^{\circ}_{P,T} - \overline{H}^{\circ}_{P_r,T_r} = \int_{T_r}^{T} \overline{C}^{\circ}_{P_r} dT + \int_{P_r}^{P} \left(\overline{V}^{\circ} - T \left(\frac{\partial \overline{V}^{\circ}}{\partial T} \right)_{P} \right)_{T} dP \,, \tag{A–15}$$

$$\overline{G}^{\circ}_{P,T} - \overline{G}^{\circ}_{P_r,T_r} = - \overline{S}^{\circ}_{P_r,T_r} (T - T_r) + \int_{T_r}^{T} \overline{C}^{\circ}_{P_r} dT - T \int_{T_r}^{T} \overline{C}^{\circ}_{P_r} d\ln T + \int_{P_r}^{P} \overline{V}^{\circ}_{T} dP \,, \tag{A–16}$$

and the partial isobaric temperature derivative of Eqn. (A-2), that we can write

$$\begin{aligned} \Delta\overline{H}^{\circ} = {} & \Delta\overline{H}^{\circ}_{f} + c_1 (T - T_r) - c_2 \left[\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right] + a_1 (P - P_r) \\ & + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) + \left(\frac{2T - \theta}{(T - \theta)^2} \right) \left(a_3 (P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right) \\ & + \omega_e \left(TY - T_r Y_{P_r,T_r} + \left(\frac{1}{\varepsilon} - 1 \right) - \left(\frac{1}{\varepsilon_{P_r,T_r}} - 1 \right) \right) , \end{aligned} \tag{A–17}$$

and

$$\Delta\overline{G}^{\circ} = \overline{G}^{\circ}_{f} - \overline{S}^{\circ}_{P_r,T_r} (T - T_r) - c_1 \left(T \ln \left(\frac{T}{T_r} \right) - T + T_r \right)$$

$$- c_2\left(\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{T_r - \theta}\right)\right]\left(\frac{\theta - T}{\theta}\right) - \frac{T}{\theta^2}\ln\left(\frac{T_r(T - \theta)}{T(T_r - \theta)}\right)\right)$$

$$+ a_1(P - P_r) + a_2 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right) + \left(\frac{1}{T - \theta}\right)\left[a_3(P - P_r) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right]$$

$$+ \omega_e\left(Y_{P_r,T_r}(T - T_r) + \left(\frac{1}{\varepsilon} - 1\right) - \left(\frac{1}{\varepsilon_{P_r,T_r}} - 1\right)\right) . \qquad \text{(A–18)}$$

Equations (A-10), (A-11), (A-17) and (A-18) are used to regress experimental data for aqueous neutral species at elevated temperatures and pressures, as well as to make predictions for many species for which experimental data are not available (Shock et al., 1989; Shock and Helgeson, 1990; Schulte and Shock, 1993; 2001; Shock, 1995; Dale et al., 1997; Schulte et al., 2001). These calculations are consistent with the approach of $\overline{C}_P^\circ$, $\overline{S}^\circ$, $\overline{V}^\circ$, and $\Delta\overline{H}_f^\circ$ of aqueous neutral species to ∞ at the critical point of H_2O.

Table 1. Summary of standard partial molal thermodynamic properties of aqueous alkyl thiols at 25°C and 1 bar, calculated with data taken from the literature.

	$\Delta\overline{G}^{\circ}_{f}$ [a]	$\Delta\overline{H}^{\circ}_{f}$ [a]	$\overline{S}^{\circ}$ [b]
methanethiol	-1840.[c]	-11650.[d]	38.60[e]
ethanethiol	-1100.[c]	-17820.[d]	45.50[e]
propanethiol	1380.[c]	-23320.[d]	53.90[e]
butanethiol	3560.[c]	-28630.[d]	61.30[e]
pentanethiol	6150.[f]		

a. cal mol^{-1} b. cal mol^{-1} K^{-1} c. Calculated from $\Delta\overline{G}^{\circ}_{f}$(g) from Alberty et al. (1987) and $\Delta\overline{G}^{\circ}_{r}$ (g↔aq) from Abraham et al. (1990) d. Calculated from $\Delta\overline{H}^{\circ}_{f}$ (g) from Stull et al. (1969) and $\Delta\overline{H}^{\circ}_{r}$(g↔aq) from Abraham et al. (1990) e. Calculated from $\Delta\overline{H}^{\circ}_{f}$ and $\Delta\overline{G}^{\circ}_{f}$ in the table, together with S° of the elements from Cox et al. (1989) f. Calculated from $\Delta\overline{G}^{\circ}_{f}$(g) from Alberty et al. (1987) and $\Delta\overline{G}^{\circ}_{r}$ (g↔aq) from Amoore and Buttery (1978) ble 2. Summary of standard partial molal thermodynamic properties of aqueous alkyl thiols at 25°C and 1 bar, together with parameters for the ised HKF equations of state (see appendix) used to calculate the same properties at high temperatures and pressures.

	$\Delta\overline{G}^{\circ}_{f}$ ^{a}	$\Delta\overline{H}^{\circ}_{f}$ ^{a}	$\overline{S}^{\circ}$ ^{b}	$\overline{C}^{\circ}_{P}$ ^{b}	$\overline{V}^{\circ}$ ^{c}	$a_1^{d} \times 10$	$a_2^{a} \times 10^{-2}$	a_3^{e}	$a_4^{f} \times 10^{-4}$	c_1^{b}	$c_2^{f} \times 10^{-4}$	$\omega_e^{a} \times 10^{-5}$
ethanethiol	-1840.^{g}	-11650.^{h}	38.60^{i}	58.70^{j}	52.97^{k}	8.5523	23.5100	-25.8188	-3.7509	62.0673	-5.5753	-0.8704
hanethiol	-1100.^{g}	-17820.^{h}	45.50^{i}	79.90^{j}	67.77^{k}	10.7143	28.3927	-26.8467	-3.9528	80.0173	-3.8792	-0.8543
opanethiol	1380.^{g}	-23320.^{h}	53.90^{i}	101.10^{l}	83.57^{l}	12.8901	33.3639	-28.1086	-4.1583	97.9674	-2.2323	-0.8382
tanethiol	3560.^{g}	-28630.^{h}	61.30^{i}	122.30^{m}	99.37^{n}	15.0522	38.2464	-29.1770	-4.3601	115.9174	-0.5357	-0.8220
entanethiol	6150.^{o}	-34530.^{p}	66.60^{i}	143.50^{m}	115.17^{n}	17.2279	43.1557	-30.2409	-4.5631	133.8675	1.1112	-0.8059
exanethiol	7930.^{q}	-40200.^{p}	73.30^{r}	164.70^{m}	130.97^{n}	19.3900	48.1004	-31.4671	-4.7675	151.8175	2.8073	-0.7898
eptanethiol	9980.^{q}	-45870.^{p}	80.00^{r}	185.90^{m}	146.77^{n}	21.5657	53.0097	-32.5313	-4.9704	169.7675	4.4542	-0.7737
ctanethiol	12030.^{q}	-51540.^{p}	86.70^{r}	207.10^{m}	162.57^{n}	23.7278	57.8922	-33.5994	-5.1723	187.7176	6.1503	-0.7576
onanethiol	14080.^{q}	-57210.^{p}	93.40^{r}	228.30^{m}	178.37^{n}	25.8899	62.8369	-34.8256	-5.3767	205.6676	7.7972	-0.7415
ecanethiol	16130.^{q}	-62880.^{p}	100.10^{r}	249.50^{m}	194.17^{n}	28.0656	67.7462	-35.8899	-5.5796	223.6177	9.4938	-0.7253
ndecanethiol	18180.^{q}	-68550.^{p}	106.80^{r}	270.70^{m}	209.97^{n}	30.2277	72.6287	-36.9579	-5.7815	241.5677	11.1407	-0.7092
odecanethiol	20230.^{q}	-74220.^{p}	113.50^{r}	291.90^{m}	225.77^{n}	32.4035	77.5999	-38.1798	-5.9870	259.5177	12.8368	-0.6931

a. cal mol^{-1} b. cal mol^{-1} K^{-1} c. cm^{3} mol^{-1} d. cal mol^{-1} bar^{-1} e. cal K mol^{-1} bar^{-1} f. cal K mol^{-1} g. Calculated from $\Delta\overline{G}^{\circ}_{f}$(g) from Alberty et al. (1987) and $\Delta\overline{G}^{\circ}_{r}$(g↔aq) from Abraham et al. (1990) h. Calculated from $\Delta\overline{H}^{\circ}_{f}$(g) from Stull et al. (1969) and $\Delta\overline{H}^{\circ}_{r}$(g↔aq) from Abraham et al. (1990) i. Calculated from $\Delta\overline{H}^{\circ}_{f}$ and $\Delta\overline{G}^{\circ}_{f}$ in the table, together with S° of the elements from Cox et al. (1989) j. Estimated by subtracting multiples of 21.2 cal mol^{-1} K^{-1} (after Shock and Helgeson, 1990) from estimated $\overline{C}^{\circ}_{P}$ of propanethiol as discussed in text k. Estimated by subtracting multiples of 15.8 cm^{3} mol^{-1} (after Shock and Helgeson, 1990) from estimated $\overline{V}^{\circ}$ of propanethiol as discussed in text l. Estimated as described in text m. Estimated by adding multiples of 21.2 cal mol^{-1} K^{-1} (after Shock and Helgeson, 1990) to estimated $\overline{C}^{\circ}_{P}$ of propanethiol. n. Estimated by adding multiples of 15.8 cm^{3} mol^{-1} (after Shock and Helgeson, 1990) to estimated $\overline{V}^{\circ}$ of propanethiol. o. Calculated from $\Delta\overline{G}^{\circ}_{f}$ (g) from Alberty et al. (1987) and $\Delta\overline{G}^{\circ}_{r}$(g↔aq) from Amoore and Buttery (1978) p. Estimated using Equation (2). q. Estimated using Equation (1) r. Estimated using Equation (3).

Table 3. Reactions describing mineral assemblages that can buffer the activities of chemical species in hydrothermal environments.

PPM

(Pyrrhotite-Pyrite-Magnetite)

$$\underset{\text{pyrrhotite}}{1.5\ FeS} + H_2O = \underset{\text{pyrite}}{0.75\ FeS_2} + \underset{\text{magnetite}}{0.25\ Fe_3O_4} + H_2$$

$$\underset{\text{pyrite}}{0.25\ FeS_2} + \underset{\text{pyrrhotite}}{0.5\ FeS} + H_2O = \underset{\text{magnetite}}{0.25\ Fe_3O_4} + H_2S$$

FMQ

(Fayalite-Magnetite-Quartz)

$$\underset{\text{fayalite}}{1.5\ Fe_2SiO_4} + H_2O = \underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{quartz}}{1.5\ SiO_2} + H_2$$

PM

(Pyrrhotite-Magnetite)

$$\underset{\text{pyrrhotite}}{3\ FeS} + 4\ H_2O = \underset{\text{magnetite}}{Fe_3O_4} + 3\ H_2S + H_2$$

Table 4. Reactions forming methanol from methanethiol and ethanol and acetic acid from ethanethiol, along with the reduced laws of mass action required to calculate the logarithms of the equilibrium activities of methanol, ethanol and acetic acid. The resulting values of the log equilibrium activities are plotted in Figure 9.

Methanol Formation

$$\underset{\text{methanethiol}}{CH_3SH} + H_2O = \underset{\text{methanol}}{CH_3OH} + H_2S$$

$$\log a_{CH_3OH} = \log K + \log a_{CH_3SH} - \log a_{H_2S}$$

Ethanol Formation

$$\underset{\text{ethanethiol}}{C_2H_5SH} + H_2O = \underset{\text{ethanol}}{C_2H_5OH} + H_2S$$

$$\log a_{C_2H_5OH} = \log K + \log a_{C_2H_5SH} - \log a_{H_2S}$$

Acetic Acid Formation

$$\underset{\text{ethanethiol}}{C_2H_5SH} + 2H_2O = \underset{\text{acetic acid}}{CH_3COOH} + H_2S + 2H_2$$

$$\log a_{CH_3COOH} = \log K - \log a_{H_2S} - 2 \log a_{H_2} + \log a_{C_2H_5SH}$$

Figure Captions

Figure 1. Standard partial molal Gibbs free energy of formation of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. The free energy values for the aqueous species were calculated from the standard Gibbs free energies of formation of the gas (Alberty et al., 1987) and the free energy of solubility reactions (Abraham et al., 1990); see Table 2 for details.

Figure 2. Standard partial molal enthalpy of formation of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. The enthalpy values for the aqueous species were calculated from the standard enthalpies of formation of the gas (Alberty et al., 1987) and the free energy of solubility reactions (Abraham et al., 1990); see Table 2 for details.

Figure 3. Standard partial molal entropy of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. See Table 2 for details of how these values were calculated.

Figure 4. Estimated values of the standard partial molal heat capacity (left-hand y-axis; open circles) and volume (right-hand y-axis; open squares) of aqueous alkyl thiols as a function of the number of carbons in the alkyl chain. Also plotted are the experimentally determined values of these properties for H_2S (Shock et al., 1992), which plot at $\bar{n} = 0$ (filled symbols).

Figure 5. Logarithm of equilibrium constants for reactions to form aqueous alkyl thiols from CO, H_2S and H_2 as a function of temperature (at saturation pressure). The general reaction is shown for reference.

Figure 6. Logarithm of equilibrium constants for reactions to form aqueous alkyl thiols from CO_2, H_2S and H_2 as a function of temperature (at saturation pressure). The general reaction is shown for reference. The letter "n," corresponding to the number on the curves, refers to the number of carbons in the alkyl chain and determines the stoichiometric reaction coefficients for various species in the reactions (e.g. '1' refers to methanethiol, '2' to ethanethiol, etc.).

Figure 7. Logarithm of methanethiol activity as a function of temperature for modern hydrothermal vent systems. The activity of H_2S and the hydrogen fugacity are set by values in equilibrium with the PPM mineral assemblage. The concentration of CO_2 (13.8 mmol) for modern systems was taken from the literature for 11-13°N EPR vent fluids (Von Damm, 1990) and the CO concentration was estimated at 10^{-6} m.

Figure 8. Logarithm of methanethiol activity as a function of temperature for early Earth hydrothermal vent systems. The activity of H_2 is set by values in equilibrium with the FMQ mineral assemblage and the activity of H_2S is set by pyrrhotite-magnetite equilibrium at the activity of H_2 from the FMQ assemblage. The activity of CO_2 and the CO are for equilibrium with 10 bars and 1 bar, respectively, of these gases in the Archaean atmosphere (after Kasting, 1993).

Figure 9. Logarithm of equilibrium constants for reactions in Table 4, forming methanol from methanethiol and ethanol and acetic acid from ethanethiol at 250 bars pressure.

Figure 10. Calculated logarithms of equilibrium activities of methanol formed from methanethiol and ethanol and acetic acid from ethanethiol as functions of temperature at 250 bars pressure. A) These values were calculated for modern hydrothermal systems assuming that the methanethiol and ethanethiol formed from CO. B) Values for modern hydrothermal systems assuming that the methanethiol and ethanethiol were formed from CO_2. C) These values were calculated for early Earth hydrothermal systems assuming the methanethiol and ethanethiol formed from CO. D) Values for early Earth hydrothermal systems assuming the methanethiol and ethanethiol formed from CO_2.

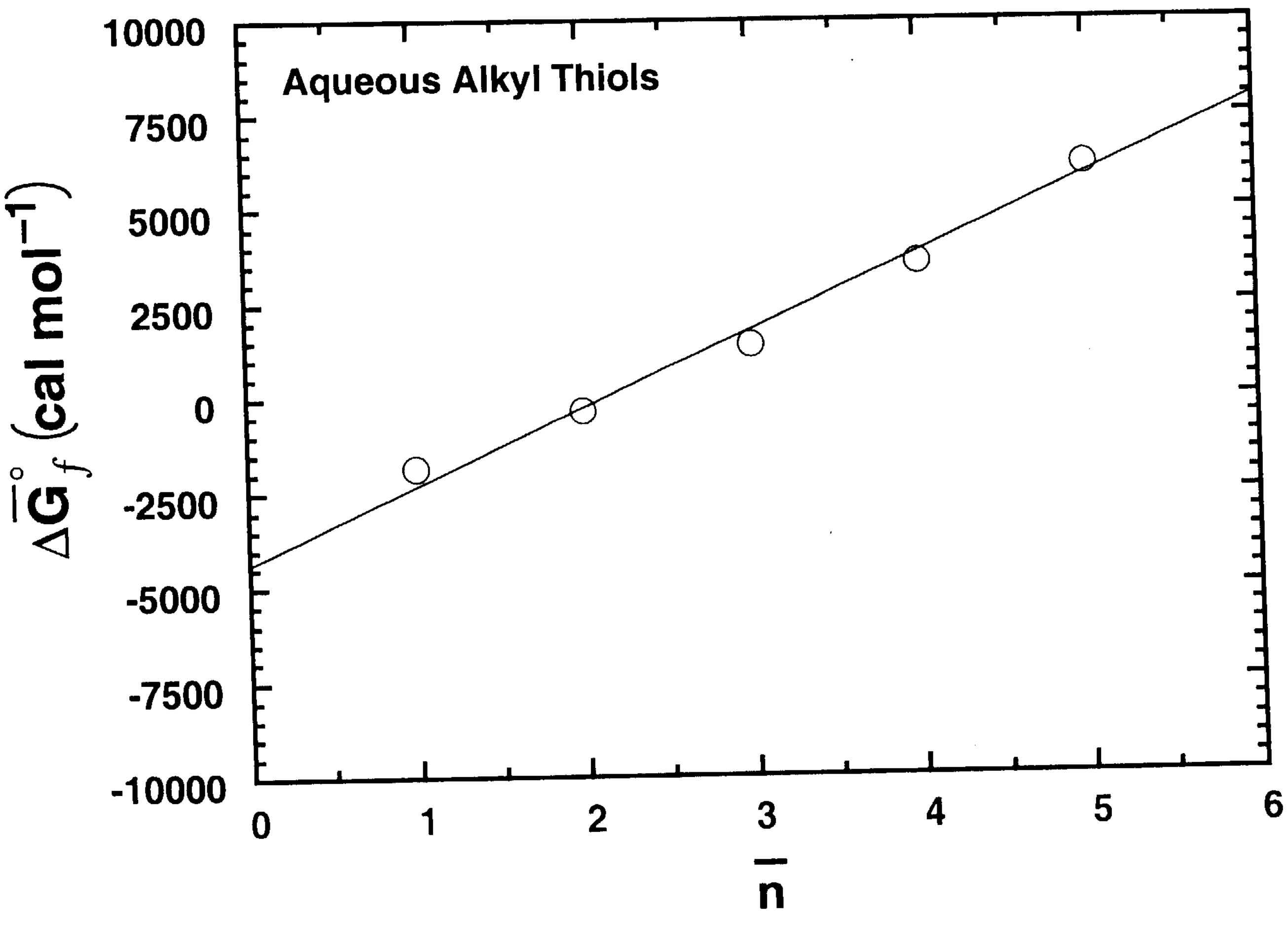

Aqueous Alkyl Thiols
$\Delta\bar{G}^{\circ}_{f}$ (cal mol^{-1})
10000
7500
5000
2500
0
-2500
-5000
-7500
-10000
0
1
2
3
4
5
6
$\bar{n}$

Figure 1

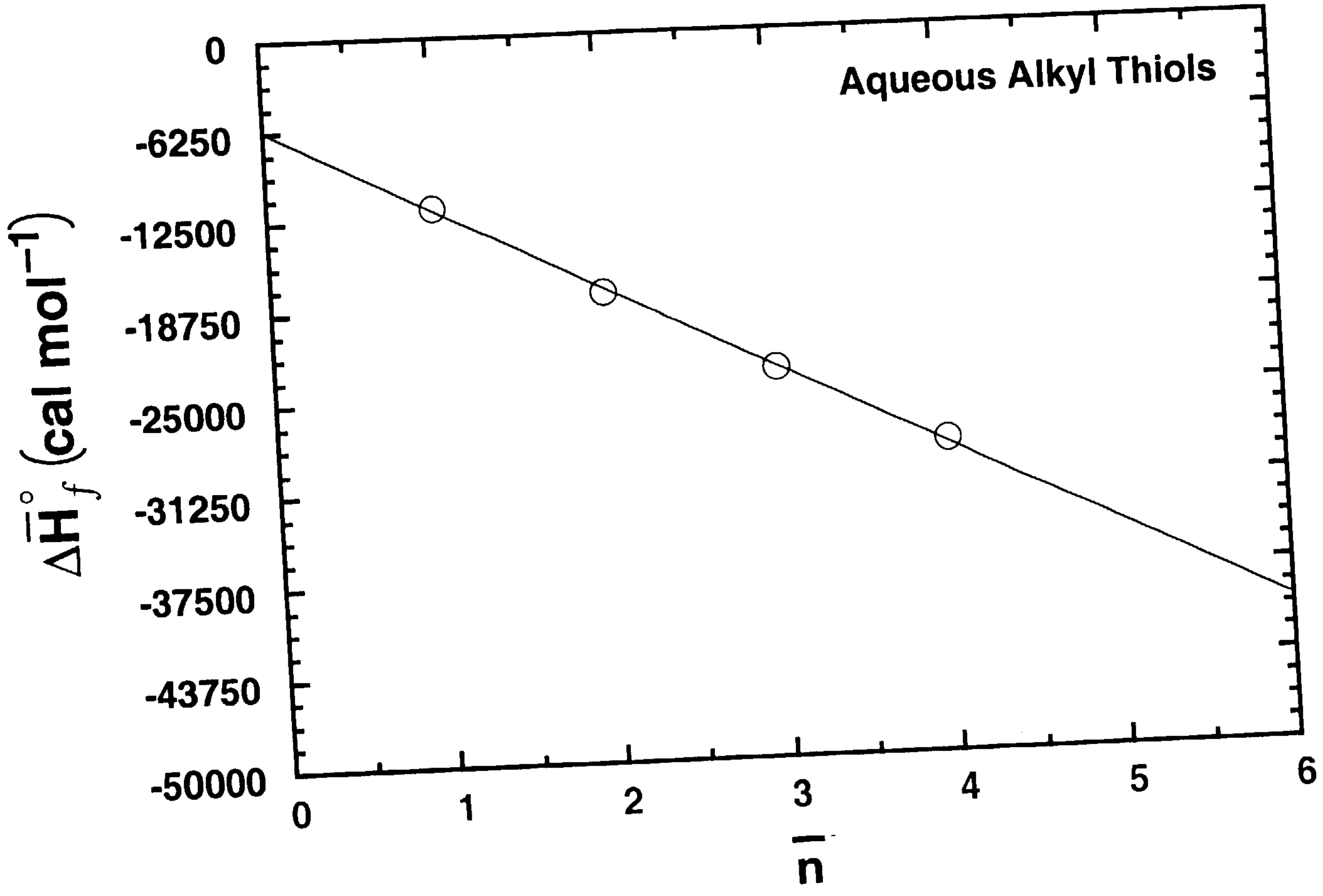

Aqueous Alkyl Thiols
$\Delta\bar{H}^{\circ}_{f}$ (cal mol^{-1})
0
-6250
-12500
-18750
-25000
-31250
-37500
-43750
-50000
0
1
2
3
4
5
6
$\bar{n}$

Figure 2

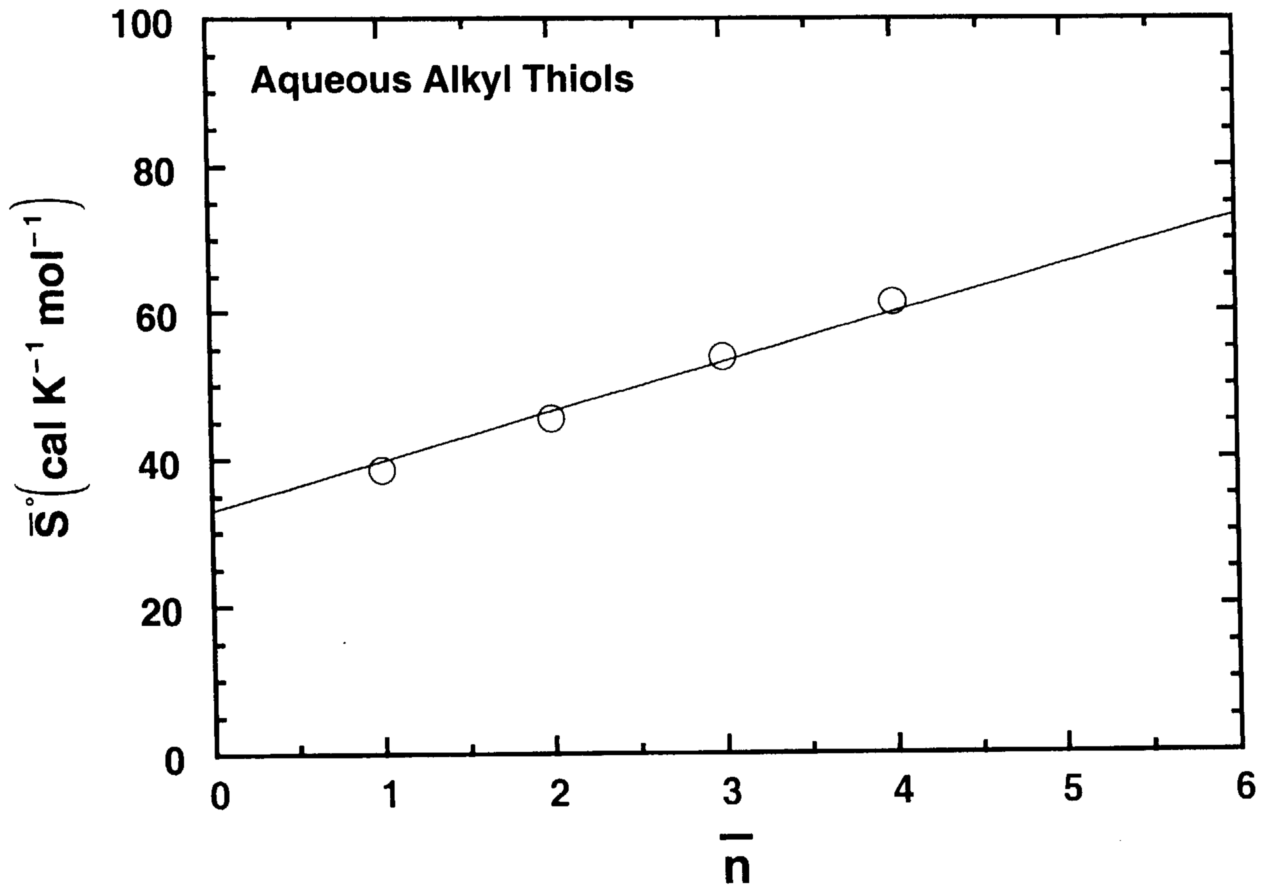
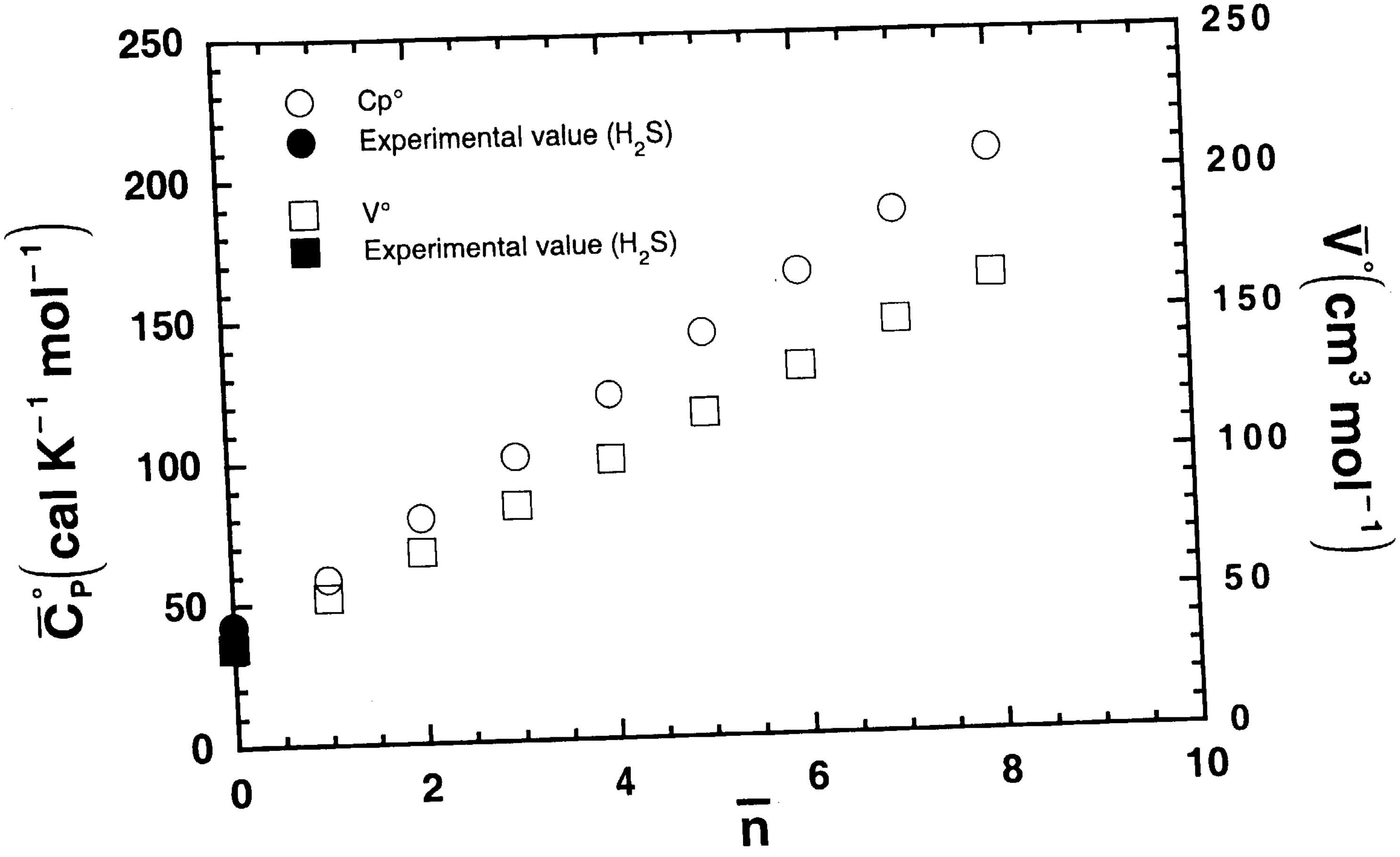

Aqueous Alkyl Thiols
$\bar{S}^{\circ}$ (cal K^{-1} mol^{-1})
100
80
60
40
20
0
0
1
2
3
4
5
6
$\bar{n}$

Figure 3



250
200
150
100
50
0
$\bar{C}_P^\circ$(cal K^{-1} mol^{-1})
○ Cp°
● Experimental value (H_2S)
□ V°
■ Experimental value (H_2S)
0
2
4
6
8
10
$\bar{n}$
250
200
150
100
50
0
$\bar{V}^\circ$(cm^3 mol^{-1})

Figure 4

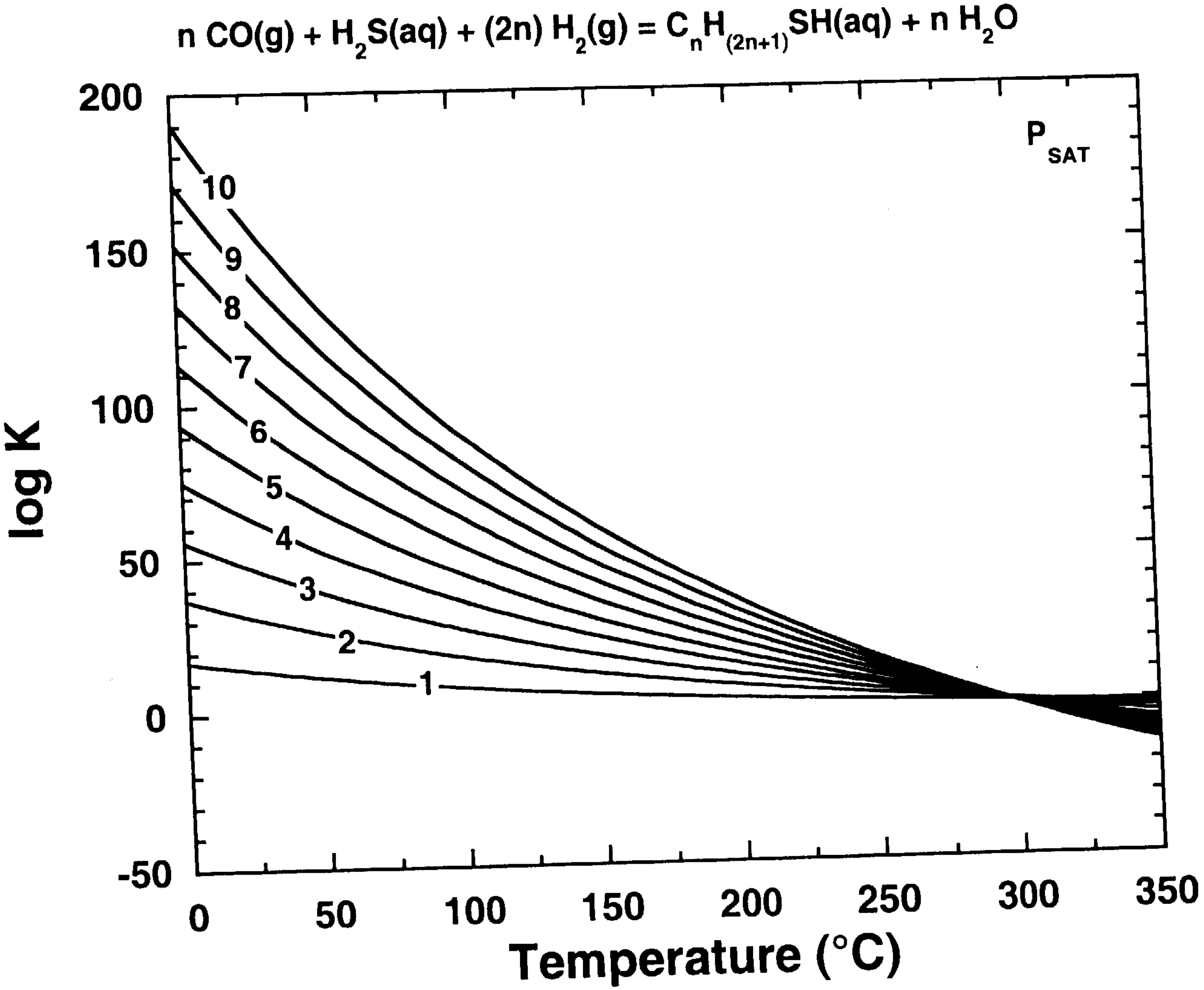
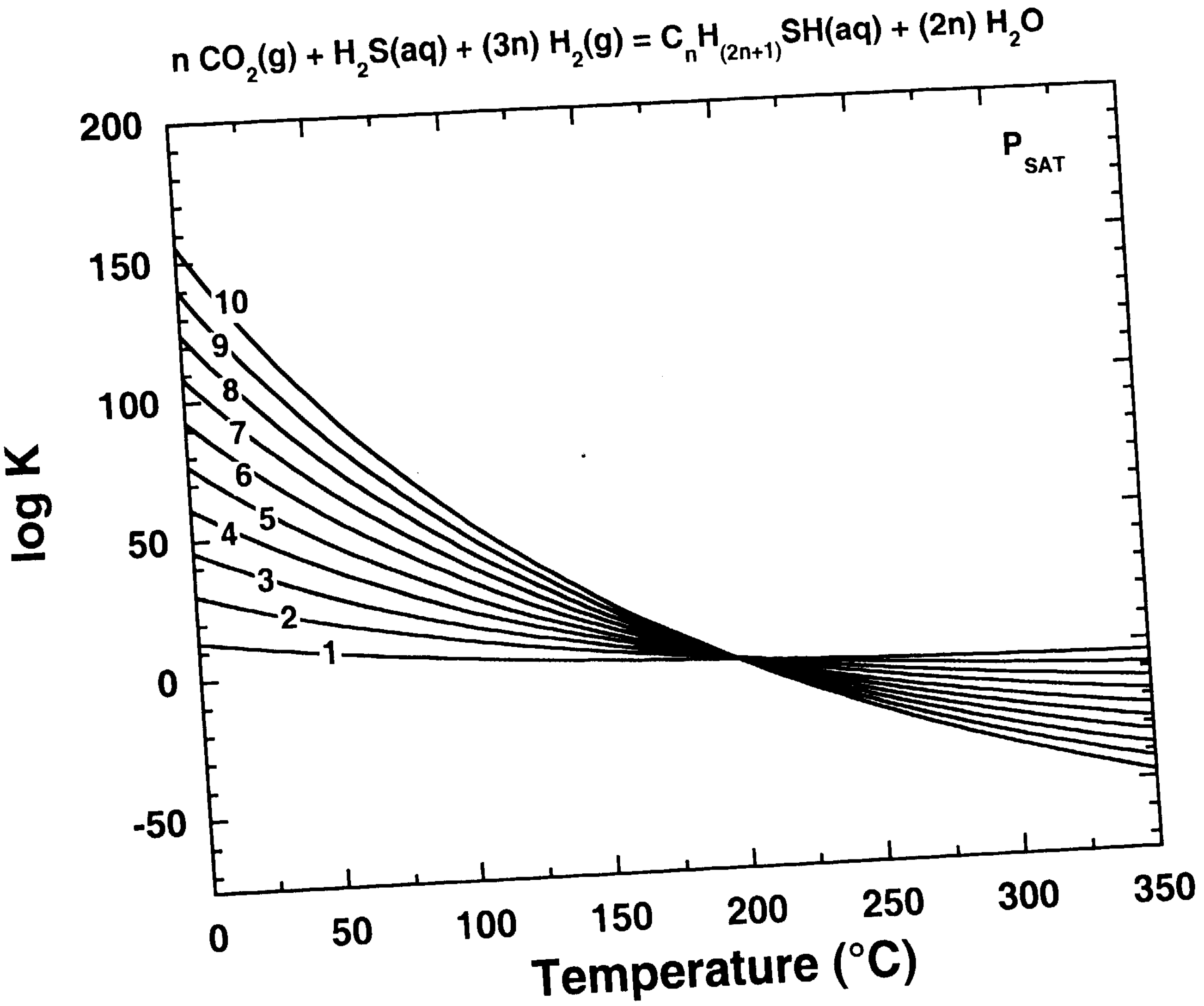
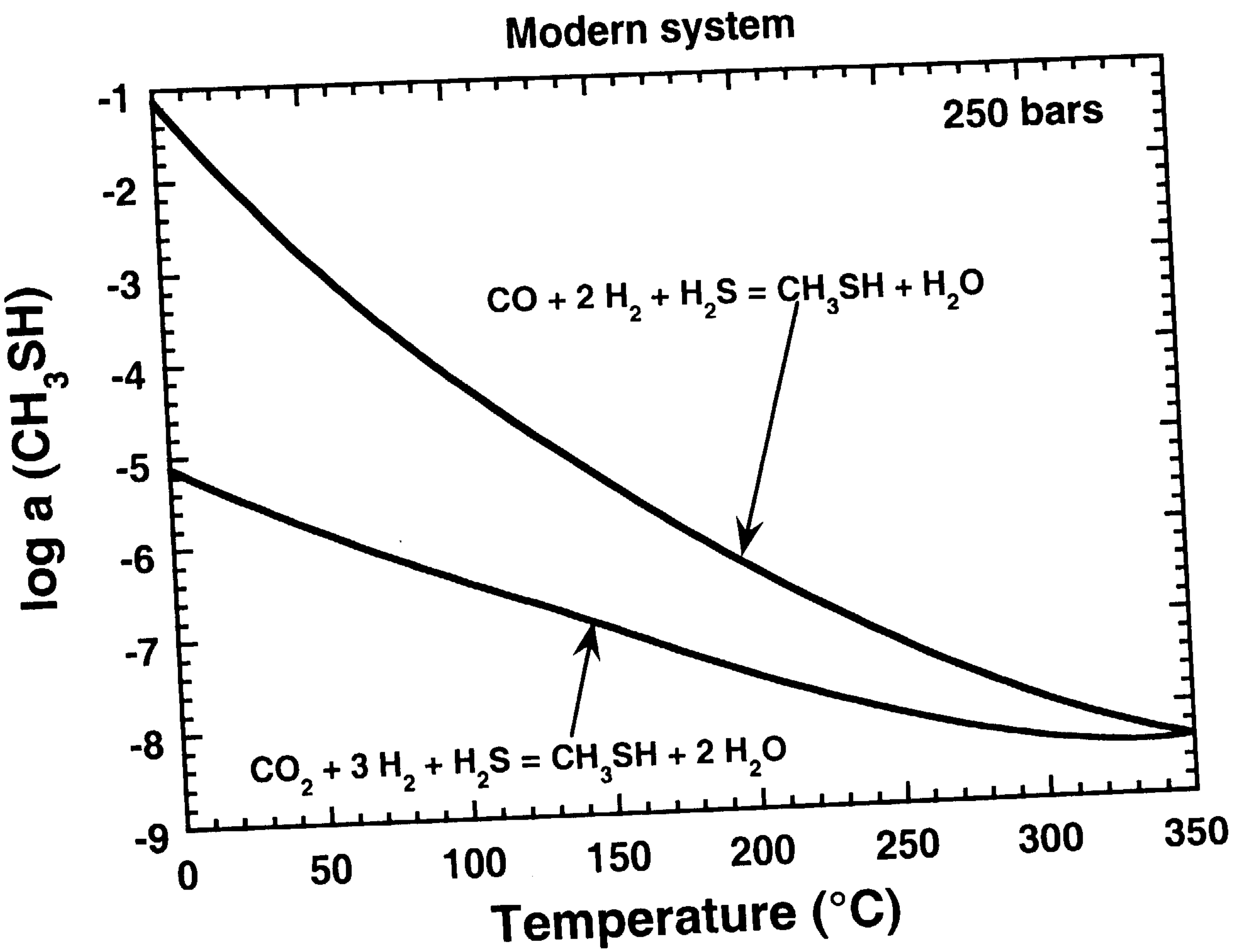

n CO(g) + H_2S(aq) + (2n) H_2(g) = $C_nH_{(2n+1)}$SH(aq) + n H_2O
P_{SAT}
log K
200
150
100
50
0
-50
Temperature (°C)
0
50
100
150
200
250
300
350
10
9
8
7
6
5
4
3
2
1

Figure 5



$n\,CO_2(g) + H_2S(aq) + (3n)\,H_2(g) = C_nH_{(2n+1)}SH(aq) + (2n)\,H_2O$

Figure 6



Modern system
250 bars
$CO + 2 H_2 + H_2S = CH_3SH + H_2O$
$CO_2 + 3 H_2 + H_2S = CH_3SH + 2 H_2O$
log a (CH_3SH)
-1
-2
-3
-4
-5
-6
-7
-8
-9
0
50
100
150
200
250
300
350
Temperature (°C)

Figure 7

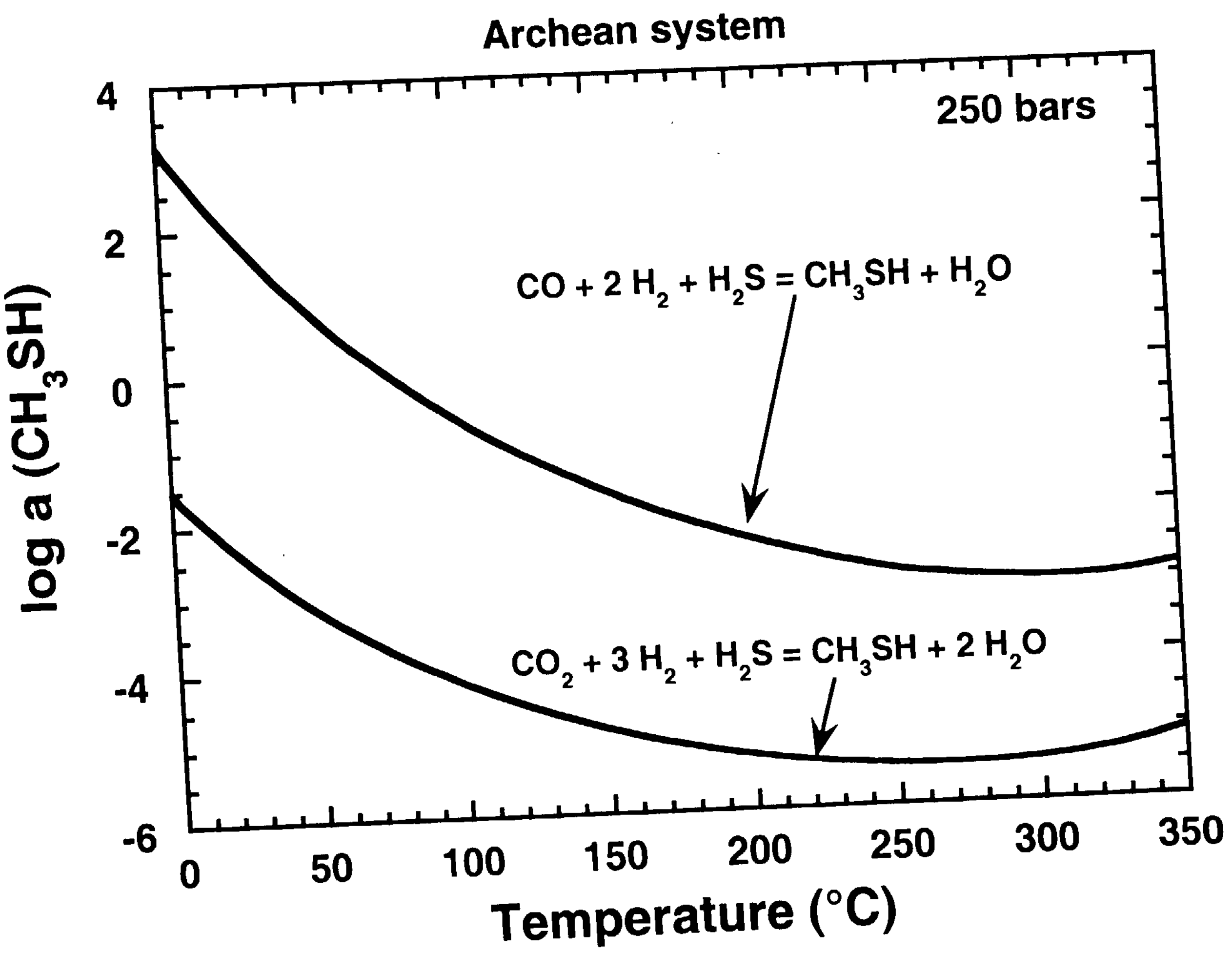

Archean system
250 bars
$CO + 2 H_2 + H_2S = CH_3SH + H_2O$
$CO_2 + 3 H_2 + H_2S = CH_3SH + 2 H_2O$
log a (CH_3SH)
4
2
0
-2
-4
-6
0
50
100
150
200
250
300
350
Temperature (°C)

Figure 8

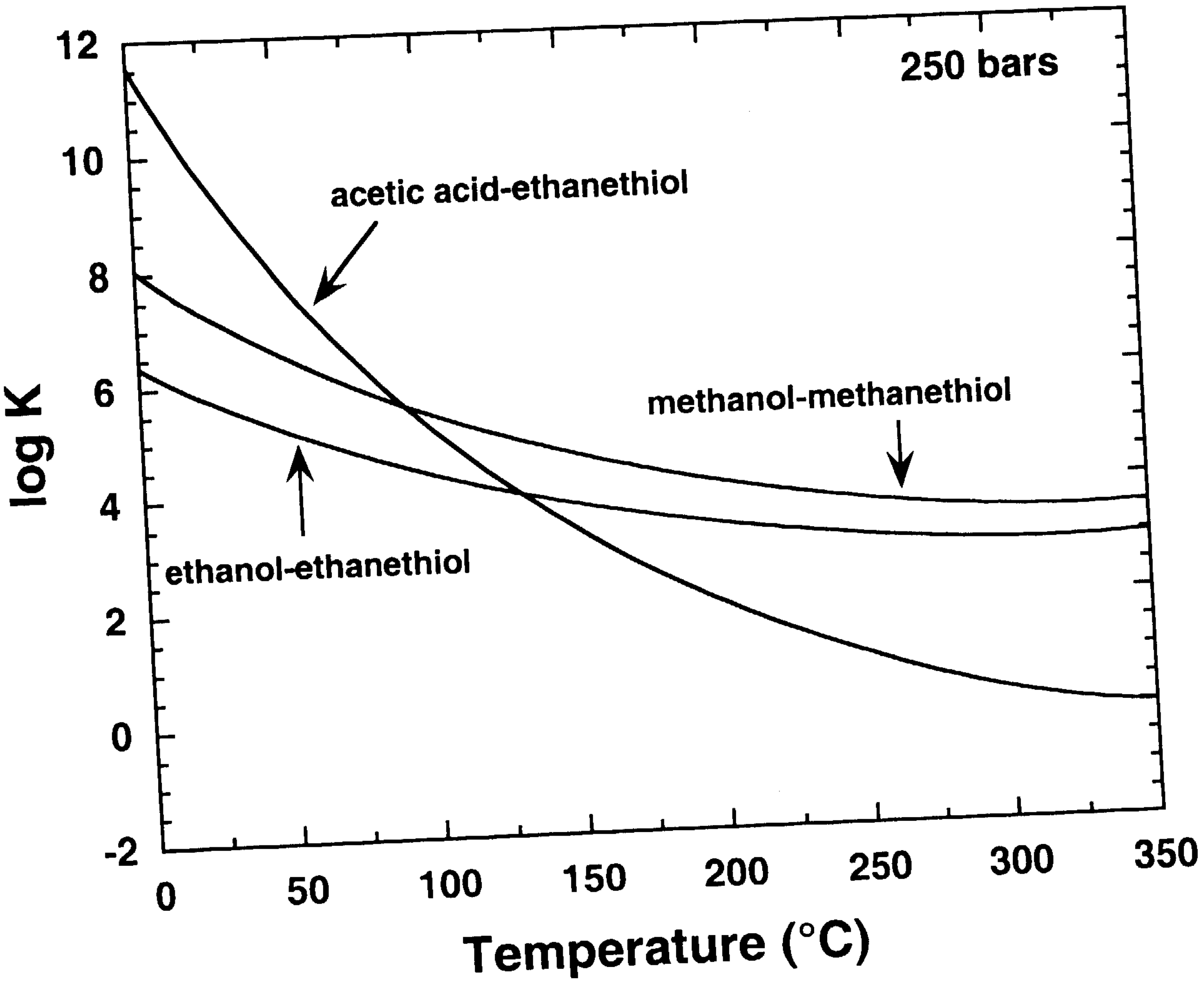

250 bars
acetic acid-ethanethiol
methanol-methanethiol
ethanol-ethanethiol
log K
12
10
8
6
4
2
0
-2
0
50
100
150
200
250
300
350
Temperature (°C)

Figure 9

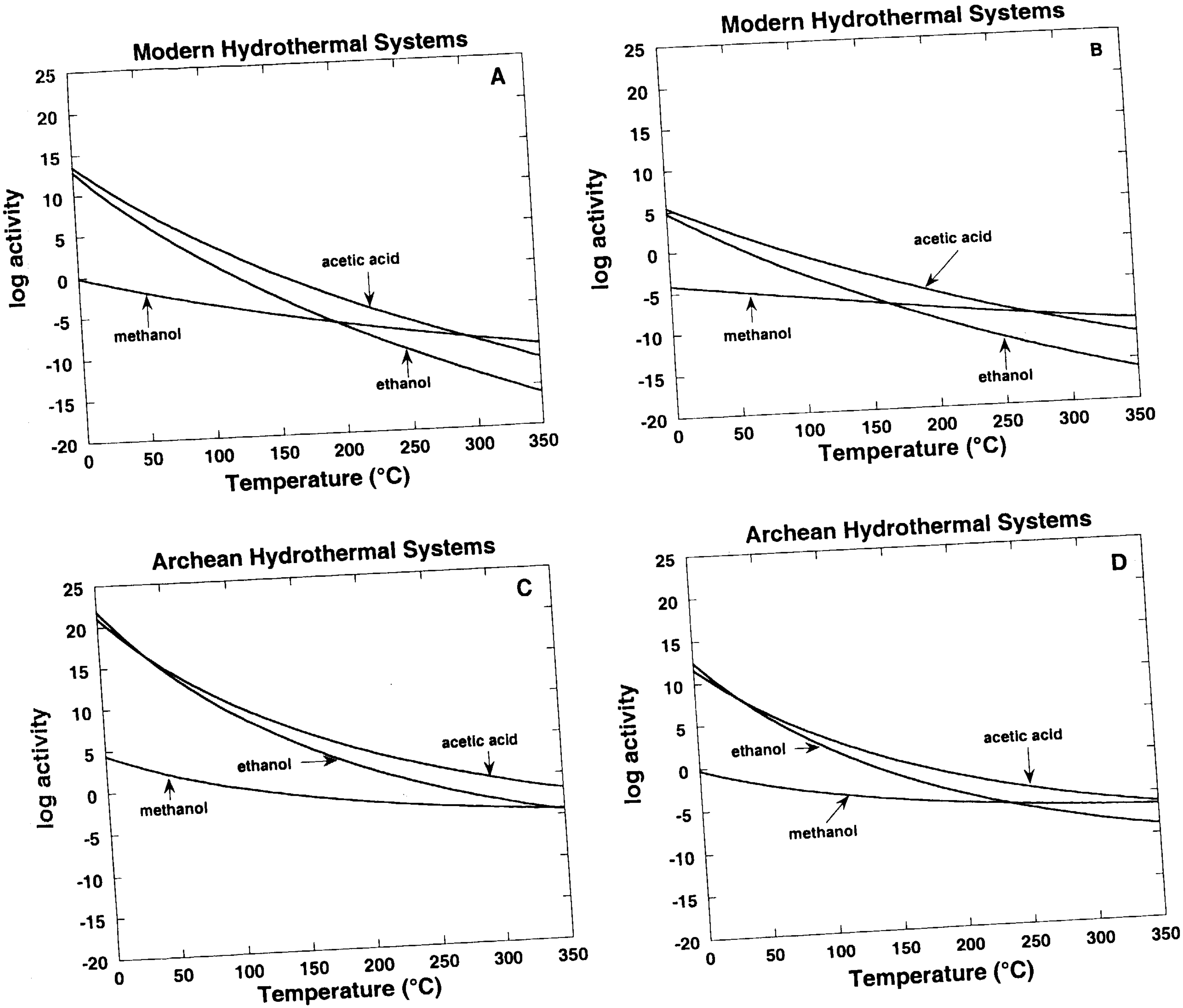

Modern Hydrothermal Systems
A
log activity
25
20
15
10
5
0
-5
-10
-15
-20
0
50
100
150
200
250
300
350
Temperature (°C)
acetic acid
methanol
ethanol
Modern Hydrothermal Systems
B
acetic acid
methanol
ethanol
Archean Hydrothermal Systems
C
acetic acid
ethanol
methanol
Archean Hydrothermal Systems
D
ethanol
acetic acid
methanol

Figure 10