[AMERICAN JOURNAL OF SCIENCE, VOL. 295, MAY, 1995, P. 496–580]

ORGANIC ACIDS IN HYDROTHERMAL SOLUTIONS: STANDARD MOLAL THERMODYNAMIC PROPERTIES OF CARBOXYLIC ACIDS AND ESTIMATES OF DISSOCIATION CONSTANTS AT HIGH TEMPERATURES AND PRESSURES

EVERETT L. SHOCK
Department of Earth and Planetary Sciences,
Washington University,
St. Louis, Missouri 63130

ABSTRACT. Experimental standard partial molal volumes, heat capacities, and entropies as well as apparent standard partial molal enthalpies and Gibbs free energies of mono- and dicarboxylic acids and their anions at low temperatures and pressures are used to generate correlations for predicting the same properties at high temperatures and pressures for 59 carboxylic and 18 hydroxyacid species with the revised Helgeson-Kirkham-Flowers (HKF) equation of state. Predicted equilibrium dissociation constants are compared with experimental values from the literature and tabulated as functions of pressure and temperature for 25 carboxylic acids and nine hydroxyacids. Close agreement between independent predictions and experimental data supports the generality of the computational techniques and the accuracy of predicted data. These results allow incorporation of a wide variety of organic acids into quantitative interpretations of geochemical processes.

INTRODUCTION

Aqueous carboxylic acids, acid anions, and metal-carboxylate complexes are integral to many geochemical processes in the atmosphere, soils, seawater, sedimentary basins, and hydrothermal systems. The carboxylic acids are commonly subdivided (Thurman, 1985) into volatile fatty acids (monocarboxylic acids with 1-5 carbon atoms per molecule), nonvolatile fatty acids (monocarboxylic acids with >5 and usually up to about 20 carbon atoms per molecule), dicarboxylic acids (with two carboxyl groups), aromatic acids (derivatives of benzene or other aromatic hydrocarbons), and hydroxyacids (carboxylic acids which also possess hydroxyl groups). In surface waters, carboxylic acids make up 5 to 8 percent of the dissolved organic carbon, with usually more than half this amount accounted for by the nonvolatile fatty acids (Thurman, 1985). Volatile fatty acids are typically at lower concentrations than nonvolatile fatty acids in surface waters but at considerably higher concentrations in oil-field brines and other sedimentary basin fluids where concentrations of volatile fatty acids approach 10,000 ppm (see below). Thermodynamic data for several members of each of these groups of aqueous carboxylic acids were reviewed in the present study, and the results described in this paper provide a set of consistent data, equations, and parameters to calculate the thermodynamic properties of 77 aqueous carboxylic acids species at temperatures and pressure through-out the crust of the Earth. Correlations found among the properties of these various groups of acids allow predictions for hundreds of other organic acids involved in geochemical processes.

The geochemical distribution of carboxylic acids.—In the atmosphere, concentrations of carboxylic acids range up to several ppb in the gas phase (Norton, 1985; Graedel, Hawkins, and Claxton, 1986; Andreae and others, 1987, 1988; Rosenberg and others, 1988; Dawson and Farmer, 1988; Puxbaum and others, 1988; Keene and others, 1989). Concentrations of carboxylic acids are generally ≤ 3 ppb in uncontaminated cloud water, fog, and precipitation, but can be up to 5 ppm in polluted environments.[1] Numerous photochemical reactions that consume or produce these acids have been proposed for the atmosphere.[2] Sources for atmospheric carboxylic acids other than photochemical reactions include the oceans (Graedel and Weschler, 1981), tobacco smoke (Sakuma and others, 1983; Guerin, 1991), automobile exhaust (Grosjean, 1989), and direct emissions from vegetation (Nicholas, 1973; Keene and Galloway, 1986; Talbot and others, 1990; Jacob and Wofsy, 1990; Servant and others, 1991) which appear to be a major source of formic, acetic, and propanoic acids to the atmosphere over rainforests. Plants and their degradation products are also thought to be the source of organic acids in soils (Robinson, 1980; Thurman, 1985), and many investigators[3] have shown increases in mineral solubility and rates of dissolution in the presence of organic acids at low temperatures.

Although organic acids in sediments and pore waters may be derived directly from planktonic and nektonic organisms (Lewis, 1969; Jeffries, 1972), benthic bacteria are known to produce and consume carboxylic acids during anaerobic fermentation of organic matter in marine sediments[4], where the combined concentration of formic, acetic, and butanoic acids may be as high as 150 ppm. Metabolic processes may also be involved in the origin and consumption of carboxylic acids found in rivers, where concentrations of volatile fatty acids can reach 500 ppb and

---

[1] Meyers and Hites (1982), Keene, Galloway, and Holden (1983), Norton, Roberts, and Huebert (1983), Likens, Edgerton, and Galloway (1983), Kawamura and Kaplan (1984, 1990, 1991), Kawamura, Steinberg, and Kaplan (1985), Keene and Galloway (1984, 1986), Weathers and others (1988), Winiwarter and others (1988).

[2] Su, Calvert, and Shaw (1980), Duce and others (1983), Chameides and Davis (1983), Atkinson and Lloyd (1984), Jacob (1986), Jacob and Wofsy (1988), Talbot and others (1988, 1990), Moortgat, Veyret, and Lesclaux (1989a,b).

[3] Gruner (1992), Graham (1941), Schalscha, Appelt, and Schatz (1967), Ong, Swanson, and Bisque (1970), Huang and Keller (1970, 1971, 1972a,b,c), Huang and Kiang (1972), Lind and Hem (1975), Schnitzer, Khan, and Kodama (1976), Graustein, Sollins, and Cromack (1977), Antweiler and Drever (1983), Surdam, Boese and Crossey (1984), Stumm and others (1985), Manley and Evans (1986), Mast and Drever (1987), Hedlund and Öhman (1988), Bennett and others (1988), Bevan and Savage (1989), Stoessell and Pittman (1990), Hinman (1990), Wogelius and Walther (1991), Fein (1991a,b), Wieland and Stumm (1992).

[4] Boon, Leeuw, and Burlingame (1978), Van Vleet and Quinn (1979), Barcelona (1980), Sansone and Martens (1981, 1982), Shaw and others (1984),Gelwicks, Risatti, and Hayes (1989), Shaw and McIntosh (1990), Pronk and others (1991).

nonvolatile fatty acids range from 5 to >500 ppb[5], in lakes, where total concentrations are generally < 200 ppb (Allen, 1968; Winfrey and Zeikus, 1979; Hama and Handa, 1980; Matsumoto, 1981; Cappenburg and others, 1982), in rainwater (Herlihy, Galloway, and Mills, 1987), in lacustrine sediments (Smith and Oremland, 1983), and in groundwater (Cooper, 1962; Lamar and Goerlitz, 1966), as well as in sewage effluent, where concentrations reach 1000 ppm (Chian and DeWalle, 1977; Barcelona, Lijestrand, and Morgan, 1980). Excluding polluted systems, carboxylic acid concentrations in natural fresh water rarely exceed 1 ppm (Thurman, 1985). Concentrations of carboxylic acids in surface seawater are generally low[6] and apparently maintained at concentrations <1 ppm by rapid bacterial consumption (Wright and Hobbie, 1966; Hobbie, Crawford, and Webb, 1968).

In contrast, concentrations of carboxylic acids and acid anions up to 10,000 ppm are reported in oil-field brines at temperatures to at least 194°C[7]. High concentrations of organic acids (up to ~500 ppm) are also reported for hot springs in diverse geological settings (Shvets and Seletskiy, 1968; Shvets, 1971; Kawamura, Nissenbaum, and Gagosian 1992) and in pore fluids from hydrothermally altered sediments at seafloor spreading centers (Martens, 1990). Hydrous pyrolysis experiments often produce carboxylic acids from source rocks at elevated temperatures and pressures[8]. It is not yet known the extent to which these compounds are generated by the experimental conditions or whether they are simply extracted from organic matter in the source rocks which can contain organic acids (Seifert, 1972; Robin and Rouxhet, 1978; Cooles, Mackenzie, and Parkes, 1987; Jaffe, Albrecht, and Oudin, 1988a,b). Similar ambiguities (see Shock and Schulte, 1990) attend reports of carboxylic acids extracted from Murchison and other carbonaceous chondrites[9]. Nevertheless, as a result of these analyses of natural samples and laboratory experiments numerous geochemical processes including diagenesis

---

[5] Mueller, Larson, and Ferretti (1960), Lamar and Goerlitz (1966), Williams (1968), Stauffer and MacIntyre (1970), Matsumoto, Ishiwatari, and Hanya (1977), Hullett and Eisenreich (1979), Matsumoto (1981), Telang, Korchinski, and Hodgson (1982).

[6] Williams (1961), Blumer (1970), Shah and Wright (1974), Wright and Shah (1975), Williams (1975), Meyers (1976, 1980), Zsolnay (1977), Wangersky and Zika (1978), Billen and others (1980), Matsumoto (1981), Hunter and Liss (1981), Steinberg and Bada (1984).

[7] Lochte, Burnam, and Meyer (1949), Gullikson, Caraway, and Gates (1961), Zinger and Kravchik (1970), Dickey, Collins, and Fajardo (1972), Willey and others (1975),Carothers and Kharaka (1978), Surdam, Boese, and Crossey (1984), Workman and Hanor (1985), Lundegard (1985), Hanor and Workman (1986), Kharaka and others (1986, 1987), Means and Hubbard (1987), Fisher (1987), Barth (1987a,b, 1991), Land, Macpherson and Mack (1988), MacGowan and Surdam (1988, 1990a,b), Fisher and Boles (1990), Moldavanyi (1990), Connolly and others (1990), Abercrombie (1991), Land and Macpherson (1992).

[8] Kawamura and Ishiwatari (1985), Kawamura and others (1986), Barth and others (1987), Lundegard and Senftle (1987), Barth, Borgund, and Hopland (1989), Thornton and Seyfried (1987), Eglinton, Curtis, and Rowland (1987), Seewald, Seyfried, and Thornton (1990), Barth and Bjorlykke (1993).

[9] Yuen and Kvenvolden (1973), Lawless and others (1974), Peltzer and Bada (1978), Lawless and Yuen (1979), Yuen and others (1984), Peltzer and others (1984), Shimoyama and others (1986).

of sediments, maturation of organic matter, generation of natural gas, and hydrothermal transport of metals have been reassessed[10].

KINETIC AND THERMODYNAMIC DATA FOR CARBOXYLIC ACIDS

Over the past decade, several investigators have studied the kinetics of reactions involving carboxylic acids (Kharaka, Carothers, and Rosenbauer, 1983; Palmer and Drummond, 1986; Drummond and Palmer, 1986; Schleusener and others, 1987, 1988; Crossey, 1991; Bell and Palmer, 1994), and it has been shown that the rate of decarboxylation of acetic acid is dependent not only on temperature but also on the presence of minerals and the composition of the reaction vessel. Results summarized by Palmer and Drummond (1986) and Drummond and Palmer (1986) show that acetic acid persists in metastable states for geologic time spans at conditions in sedimentary basins. Other carboxylic acids are also metastably preserved in the subsurface, and it has been shown that ratios of acetic and propanoic acids are consistent with homogeneous metastable equilibrium at petroleum reservoir conditions (Shock, 1988, 1989, 1994a). As a result, it has been proposed that ratios of carboxylic acids in sedimentary basin brines can be used as tracers of the redox conditions that prevail in petroleum reservoirs and source rocks (Shock, 1988, 1989, 1990, 1994a; Helgeson and Shock, 1988; Helgeson, Knox, and Shock, 1991; Helgeson and others, 1993).

Much of the thermodynamic data for aqueous carboxylic acids is summarized in tables presented below. There are numerous other studies yielding complementary values of compressibility, enthalpy of solution, enthalpy of dilution, solubility, activity coefficients, diffusion coefficients, and other properties for these same acids[11]. These data are supplemented by studies of these acids in mixed solvents[12], electrolyte

---

[10] Surdam, Boese, and Crossey (1984), Crossey, Frost, and Surdam (1984), Lundegard, Land, and Galloway (1984), Giordano (1985, 1990), Surdam and Crossey (1985), Crossey, Surdam, and Lahann (1986), Sverjensky (1986), Giles and Marshall (1986), Edman and Surdam (1986), Drummond and Palmer (1986), Mast and Drever (1987), Lundegard and Land (1986, 1989), Lundegard and Senftle (1987), Surdam and MacGowan (1987), Hennet, Crerar, and Schwartz (1988), Shock (1988, 1989), Surdam and others (1989), Shock and Sverjensky (1989), Bevan and Savage (1989), Giles and deBoer (1989, 1990), Lundegard and Kharaka (1990), MacGowan and Surdam (1990a,b), Stoessell and Pittman (1990), Land and Macpherson (1992), Harrison and Thyne (1992), Shock and Koretsky (1993, 1995), Helgeson and others (1993), Shock (1994a).

[11] Reyher (1888), Richards and Gucker (1925), Ramsperger and Porter (1926), Richards and Mair (1929), Bury and Davies (1932), Campbell and Campbell (1934), Edsall (1935), Ralston and Hoerr (1942), Waring (1952), Crawford and Magill (1954), Hansen, Miller, and Christian (1955), Ives and Prasad (1970b), Lindenbaum (1971), Chawla and Ahluwalia (1975), Høiland and Vikingstad (1976), Mandal and others (1978), Harris, Thompson, and Wood (1980), De Lisi and others (1981), Gomez, Font, and Soler (1986), Apelblat (1986), Noulty and Leaist (1987), Strong and others (1988), Semmler and Irish (1988), Dobrogowska, Hepler, and Apelblat (1990), Apelblat and Manzurola (1990), Benoit, Louis, and Frechette (1991), Fischer and Warneck (1991), and Basaran and others (1991), among others.

[12] Schwartzenbach (1933), Harned and Embree (1935), Eisen and Joffe (1966), Chueh (1974), Arnett and others (1976), Sahay and others (1981), Choudhury and Ahluwalia (1982a), Papadopoulos and Avranas (1990), Bender, Heintz, and Lichtenthaler (1991).

solutions[13], D_2O and studies of deuterated acids[14], and studies of the pure acids and carboxylate salts[15].

In addition to the aqueous organic acids considered below, thermodynamic data for many others are available at or near 25°C and 1 bar. These measurements include heat-capacities, densities, heats of solution, heats of dilution, and dissociation constants[16]. Similar thermodynamic studies have been conducted on a wide variety of halogenated carboxylic acids which are generally anthropogenic and may persist as contaminants in many aqueous systems[17]. Other investigators, motivated in part by practical needs in the battle against corrosion during the steam generation of electricity, have determined thermodynamic properties of organic acids and their reactions in the vapor phase[18].

Experimental data for organic acids in solution and in the vapor phase are used extensively in theoretical advances and in development of empirical correlations that allow estimation of thermodynamic properties that have not been measured[19]. The present communication falls into the latter category with particular attention paid to estimation of data at high temperatures and pressures. Various theoretical methods have been applied to extend the available thermodynamic data, especially equilibrium constants for dissociation reactions, to elevated temperatures and pressures (Lindsay, 1980; Smith, Popp, and Norman, 1986; Hennet, Crerar, and Schwartz, 1988; Shock and Helgeson, 1990; DeRobertis and

[13] Kolthoff and Bosch (1982a,b, 1932), Larsson and Adell (1931a), Larsson (1932), MacDougall and Blumer (1933), Kaye and Parks (1934), Harned and Hickey (1937a,b), Morrison (1944), Kilpatrick and Eanes (1953), Stern and others (1979), Backlund and others (1981), Willard, Sullivan, and Kim (1982), Carmona and Garcia-Ramos (1985), Bonner (1988), Esteso and others (1989a,b,c), Biedermann and Molin (1989), Mesmer and others (1989), Gilkerson and Mixon (1990).

[14] Glasoe and Long (1960), Streitweiser and Klein (1963), Glasoe and Hutchinson (1964), Gary, Bates, and Robinson (1965), Paabo, Bates, and Robinson (1966), Snell and Greyson (1970).

[15] Martin and Andon (1982), Franzosini, Plautz, and Westrum (1983),Domalski, Evans, and Hearing (1984), Bernardo-Gil, Esquível and Ribeiro (1990), Domalski and Hearing (1990), Ngeyi, Malik, and Westrum (1990), Fukai, Matsuo, and Suga (1991), among others.

[16] Ives, Linstead, and Riley (1933), Jeffrey and Vogel (1936, 1939),Baker, Dippy, and Page (1937), Dippy and Lewis (1937a), German, Jeffrey, and Vogel (1937), Saxton and Waters (1937), Hartman (1938), Kilpatrick and Morse (1953), Dippy, Hughes, and Laxton (1954), Howell and Fisher (1958), Eden and Bates (1959), Klingenberg, Thole, and Lingg (1966), Ong, Douglas, and Robinson (1966), Öjelund and Wadsö (1967), Bottei and Joern (1968), Purdie, Tomson, and Riemann (1972), Strong, Blubaugh, and Cavalli (1981), Diebler, Secco, and Venturini (1984), Strong and others (1985), Perez-Camino and others (1985), Morawetz and Choi (1986), among many others.

[17] Kurz and Farrar (1969), Teng and Lenzi (1975), Bonner and Prichard (1979), Bonner (1982), Strong, Van Waes, and Doolittle (1982), Strong, Brummel, and Lindower (1987), Samploi, Marziano, and Tortato (1989), Tamaki, Ohara, and Watanabe (1989), Strehlow and Hildebrandt (1990), Hu and others (1991), Helgeson (1992).

[18] Ramsperger and Porter (1928), Fredenhagen and Liebster (1932), Bedrosian and Cheh (1974), Calis-Van Ginkel and others (1978), DeKruif and Oonk (1979), DeKruif and Blok (1982), DeWit and others (1983), Panagiotopoulos, Willson, and Reid (1988).

[19] Butler and Ramchandani (1935), Butler (1937), Kirkwood and Westheimer (1938), Westheimer and Kirkwood (1938), Hepler (1965), Høiland (1974b), Hine and Mookerjee (1975), Nichols and others (1976b), Zana (1977), Cabani, Conti, and Matteoli (1978), Cabani and Gianni (1979), Cabani and others (1981), Blandamer, Burgess, and Duce (1981), Gianni, Mollica, and Lepori (1982), Taft (1983), Oldham (1987), Shock and Helgeson (1990), Helgeson (1992).

others, 1990; Harrison and Thyne, 1992). Nevertheless, the available experimental and predicted data are insufficient for performing calculations that include the wide variety of organic acids found in geologic fluids. Lack of data also inhibits examination of the effects of changes in pH and oxidation state on the distribution of organic acids in aqueous solution during geochemical processes.

It is the purpose of this paper to present a summary of the available experimental standard partial molal thermodynamic data for aqueous mono- and dicarboxylic acids and acid anions and describe methods used to estimate these data at elevated temperatures and pressures. These methods allow prediction of dissociation constants over wide ranges of temperature and pressure encountered in geochemical processes. Results of regression of experimental data are used to construct correlation algorithms to estimate equation of state parameters for the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Helgeson, Kirkham, and Flowers, 1981; Tanger and Helgeson, 1988; Shock and others, 1992) and are consistent with correlations, parameters, and data reported by Shock and Helgeson (1988, 1990), Shock, Helgeson, and Sverjensky (1989), Sassani and Shock (1990, 1992), Shock (1992b, 1993, 1994b, 1995), Shock and Koretsky (1993, 1995), Schulte and Shock (1993), Shock and McKinnon (1993), Shock and others (1995), Willis and Shock (1995), Haas, Shock, and Sassani (1995), and Sverjensky, Shock, and Helgeson (1995).

STANDARD PARTIAL MOLAL DATA AT 25°C AND 1 BAR

Numerous investigators have measured thermodynamic properties of aqueous carboxylic acids and/or carboxylate electrolytes at 25°C and 1 bar. In addition, many determinations of thermodynamic properties for dissociation reactions have been determined at the same temperature and pressure. Some of these data are included in compilations[20]. Because a majority of data on aqueous carboxylic acids and acid anions are collected at 25°C and 1 bar, these data are reviewed in this section. Correlations among these data are also described and used to estimate values that have not been measured. Data at other temperatures are reviewed below in the context of regression with the revised-HKF equation of state. The discussion of data at 25°C and 1 bar begins with a review of data for standard partial molal volumes ($\bar{V}^\circ$) and heat capacities ($\bar{C}_P^\circ$).

$\bar{V}^\circ$ and $\bar{C}_P^\circ$.—Values of $\bar{V}^\circ$ and $\bar{C}_P^\circ$ taken from the literature for aqueous carboxylic acids and acid anions at 25°C and 1 bar are summarized in table 1. The first entry of either $\bar{V}^\circ$ and $\bar{C}_P^\circ$ for each species in table 1 corresponds to the value adopted in the present study. Most of the data selected in the present study comes from recent experimental studies in which the authors have compared their measurements with results

---

[20] Dippy (1939), Bjerrum, Schwarzenbach, and Sillén (1957), Kortüm, Vogel, and Andrussow (1961), Larson and Hepler (1969), Christensen, Hansen, and Izatt (1976), Serjeant and Dempsey (1979), Cabani and others (1981), and Høiland (1986).

TABLE 1

Standard partial molal volumes and heat capacities of aqueous carboxylic acid species at 25°C and 1 bar from experimental measurements

Species	$\bar{V}^{\circ a}$	$\bar{C}_P^{\circ b}$
formic acid	$34.69^{c,z}$, 34.7^{g}, 35.0^{x}	$22.8^{d,f}$, 19.0^{l}, 21.5^{y}, 16.97^{ak}, 20.2^{an}
acetic acid	52.01^{c}, 51.9^{g}, 51.3^{x}, 51.93^{z}, 51.94^{aa}, 51.83^{ab}, 51.66^{ah}, 51.8^{ba}	40.56^{e}, $39.4^{d,f}$, 42.0^{y}, 38.0^{ak}, 36.8^{an}, 43.8^{at}, 39.9^{az}
propanoic acid	67.9^{g}, 67.6^{x}, 67.8^{ba}	$60.5^{d,f}$, 56.0^{l}, 58.8^{y}, 63.1^{ak}, 59.3^{an}, 61.4^{az}
n-butanoic acid	84.61^{c}, 84.6^{g}, 83.9^{x}, 84.52^{ax}	$80.5^{d,f}$, 75.5^{y}, 84.85^{ak}, 78.9^{an}
n-pentanoic acid	100.5^{g}	$103.3^{d,f}$
n-hexanoic	116.55^{c}	
2-methylpropanoic		79.8^{f}, 99.9^{ap}
2-methylbutanoic	100.5^{g}	
3-methylbutanoic	100.5^{g}	
2,2-dimethylpropanoic	100.5^{g}	99.7^{f}
benzoic acid	98.77^{i}, 98.8^{al}	88.9^{h}
formate	26.16^{k}, 26.27^{ae}, 26.0^{af}, 26.26^{v}, 25.71^{av}, 26.17^{ay}	-22.0^{l}, -21.0^{ac}, $-14.^{ad}$
acetate	40.5^{l}, 40.6^{e}, $40.34,^{k,ay}$ 40.46^{ae}, 40.4^{af}, 40.68^{ab}, 40.42^{v}, 40.29^{as}, 39.86^{av}	6.2^{l}, 0.4^{ad}, 7.6^{as}
propanoate	54.95^{k}, 54.0^{ae}, 54.6^{af}, $54.82^{v,au}$, 53.93^{av}	30.9^{l}, 31.6^{ad}
n-butanoate	$70.3^{k,ay}$, 70.4^{ae}, 70.43^{v}, 69.52^{av}	44.5^{j}
n-pentanoate	86.31^{k}, 86.25^{v},86.1^{af}	70.3^{j}
n-hexanoate	102.21^{k}, 101.69^{v}, 101.5^{af}	
n-heptanoate	116.91^{v}	
n-octanoate	133.8^{u}, 133.25^{as}	$128.^{u}$, 132.6^{as}
n-decanoate	165.19^{r}	$175.^{r}$, 174.7^{aw}
n-dodecanoate	196.1^{u}	210.8^{u}
2,2-dimethylpropanoate	83.8^{af}	
benzoate	87.03^{m}	51.41^{m}, 50.9^{r}
p-toluate	100.12^{am}	65.5^{w}
phenylacetate	101.72^{aq}	63.9^{ar}
phenylpropanoate	117.93^{aq}	77.4^{ar}
phenylbutanoate	133.51^{aq}	92.0^{ar}
phenylpentanoate	149.65^{aq}	111.4^{ar}
oxalic acid	49.43^{r}, 49.12^{n}	22.7^{r}
malonic acid	66.82^{r}, 67.22^{n}	38.4^{r}, 0.2^{ai}
succinic acid	82.44^{r}, 82.94^{n}, 82.67^{ag}, 82.75^{ah}	53.3^{r}, 53.8^{s}
glutaric acid	98.98^{r}, 99.14^{n}, 98.05^{aj}	64.1^{r}, 64.8^{s}, 37.2^{ai}
adipic acid	115.15^{r}, 115.66^{n}	80.1^{r}, 80.3^{s}
pimelic acid	131.93^{n}, 131.78^{aj}	98.0^{s}
H-oxalate^{-1}	42.36^{p}, 42.32^{k}	
H-malonate^{-1}	57.07^{q}	
H-succinate^{-1}	69.99^{q}	
H-glutarate^{-1}	85.88^{q}	
H-adipate^{-1}	102.09^{1}	
H-pimelate^{-1}	117.70^{1}	
oxalate^{-2}	30.30^{q}, 30.24^{v}	
malonate^{-2}	38.43^{q}	
succinate^{-2}	$56.32^{q,v}$	
glutarate^{-2}	$72.20^{q,v}$	
adipate^{-2}	$88.46^{q,v}$	
pimelate^{-2}	104.06^{q}	
suberate^{-2}	119.83^{v}	
subacate^{-2}	151.13^{v}	

of earlier studies. In general, there is considerable close agreement among experimental determinations of $\bar{V}^\circ$ and $\bar{C}_p^\circ$ for aqueous carboxylic acids and electrolytes at 25°C and 1 bar. Typical uncertainties associated with experimental techniques as well as those attending the extrapolation of data to the standard state are evaluated by Shock and Helgeson (1988, 1990). These authors also provide an account of the uncertainties arising

---

Table 1 footnote: [a] cm^3 mol^{-1}, [b] cal mol^{-1} K^{-1}, [c] Høiland (1986), [d] Cabani and others (1981), [e] Allred and Woolley (1981), [f] Konicek and Wadsö (1971), [g] Palma and Morel (1976), [h] Guthrie (1977), [i] Desnoyers and Ichhaporia (1969), [j] Calculated from the value of $\Delta\bar{C}_p^\circ$ for the acid dissociation reaction given by Larson and Hepler (1969), together with the selected values of $\Delta\bar{C}_p^\circ$ for the aqueous acid given in the table (see text), [k] Calculated from the value of $\bar{V}^\circ$ for the aqueous sodium salt given by Høiland (1986), together with the value of $\bar{V}^\circ$ for Na^+ taken from Shock and Helgeson (1988), [l] Shock and Helgeson (1990) from regression of data for standard molal properties as functions of temperature, [m] Calculated from the property of the aqueous sodium electrolyte given by Desnoyers and others (1973), together with the property of Na^+ taken from Shock and Helgeson (1988), [n] Høiland (1975), [p] Calculated from the value of $\bar{V}^\circ$ for the aqueous potassium salt given by Høiland (1975), together with the value of $\bar{V}^\circ$ for K^+ taken from Shock and Helgeson (1988), [q] Calculated from the value of $\bar{V}^\circ$ for the aqueous sodium electrolyte given by Høiland (1975), together with the value of $\bar{V}^\circ$ for Na^+ taken from Shock and Helgeson (1988), [r] Sijpkes and others (1989), [s] Nichols and others (1976a), [t] Calculated from the value of $\bar{V}^\circ$ or $\bar{C}_p^\circ$ of the sodium electrolyte given be De Lisi, Perron and Desnoyers (1980) together with the value of $\bar{V}^\circ$ or $\bar{C}_p^\circ$ of Na^+ from Shock and Helgeson (1988), [u] Calculated from the value of $\bar{V}^\circ$ or $\bar{C}_p^\circ$ of the sodium electrolyte given by Rosenholm, Grigg and Hepler (1986) together with the value of $\bar{V}^\circ$ or $\bar{C}_p^\circ$ of Na^+ from Shock and Helgeson (1988), [v] Calculated from $\bar{V}^\circ$ for the aqueous sodium electrolyte given by Sakurai (1973), together with $\bar{V}^\circ$ for Na^+ taken from Shock and Helgeson (1988), [w] Calculated from $\bar{C}_p^\circ$ for the aqueous sodium electrolyte given by Perron and Desnoyers (1979), together with $\bar{C}_p^\circ$ for Na^+ from Shock and Helgeson (1988), [x] Daniel and Cohn (1936), [y] Rüterjans and others (1969), [z] King (1969), [aa] Redlich and Nielson (1942), [ab] Wirth (1948), [ac] Wagman and others (1982), [ad] Calculated from $\bar{C}_p^\circ$ for the aqueous sodium electrolyte from Rüterjans and others (1969) together with $\bar{C}_p^\circ$ for Na^+ from Shock and Helgeson (1988), [ae] Millero (1971), [af] Calculated from the value for $\bar{V}^\circ$ of the aqueous potassium electrolyte from Palma and Morel (1976), together with $\bar{V}^\circ$ for K^+ from Shock and Helgeson (1988), [ag] Lo Surdo, Shin, and Millero (1978), [ah] Manzurola and Apelblat (1985), [ai] Kawaizumi, Noguchi and Miyahara (1977), [aj] Apelblat and Manzurola (1989), [ak] Cohn and Edsall (1943), [al] Read (1981), [am] Calculated from the value of $\bar{V}^\circ$ from the aqueous sodium electrolyte given by Perron and Desnoyers (1979), together with $\bar{V}^\circ$ for Na^+ from Shock and Helgeson (1988), [an] Ackermann and Schreiner (1958), [ap] Kresheck and Benjamin (1964), [aq] Calculated from the value of $\bar{V}^\circ$ for the aqueous sodium electrolyte given by Ostiguy and others (1977), together with $\bar{V}^\circ$ for the Na^+ from Shock and Helgeson (1988), [ar] Calculated from the value of $\bar{C}_p^\circ$ for the aqueous sodium electrolyte given by Ostiguy and others (1977), together with $\bar{C}_p^\circ$ for Na^+ from Shock and Helgeson (1988), [as] Calculated from the value of $\bar{V}^\circ$ for the aqueous sodium electrolyte given by Leduc and Desnoyers (1973), together with $\bar{V}^\circ$ for Na^+ from Shock and Helgeson (1988), [at] Vasil'ev and others (1977), [au] Calculated from $\bar{V}^\circ$ for the aqueous sodium electrolyte given by Lucas and Le Bail (1976), together with $\bar{V}^\circ$ for Na^+ from Shock and Helgeson (1988), [av] Calculated from $\bar{V}^\circ$ from the aqueous sodium electrolyte given by Watson and Felsing (1941), together with $\bar{V}^\circ$ for Na^+ from Shock and Helgeson (1988), [aw] Calculated from data for the sodium electrolyte given by Choudhary and Ahluwalia (1982b) at 20° and 30°C together with the value of $\bar{C}_p^\circ$ for Na^+ Shock and Helgeson (1988), [ax] Calculated from data given by King (1969), [ay] Calculated from data for the sodium electrolyte given by King (1969), together with $\bar{V}^\circ$ for Na^+ from Shock and Helgeson (1988), [az] Makhatadze and Privalov (1990), [ba] Makhatadze, Medvedkin, and Privalov (1990).

from correlations among standard partial molal properties and equation of state parameters and provide algorithms which minimize uncertainty in estimated data.

Despite the wealth of experimental measurements at 25°C and 1 bar summarized in table 1, it is evident that volumetric and calorimetric measurements for many aqueous carboxylic acids are lacking. In the absence of experimental data, estimates can be made by taking advantage of the systematic behavior among the members of the various families of aqueous carboxylic acids, and through analogies drawn to other families of aqueous organic compounds. For example, it can be seen in figure 1A that values of $\overline{V}°$ for aqueous monocarboxylic acids and monocarboxylate anions correlate with the number of moles of carbon in one mole of the compounds ($\overline{n}$). The correlations indicated in figure 1A are consistent with

$$\overline{V}° = 15.8\,\overline{n} + 21.0 \tag{1}$$

for the neutral monocarboxylic acid molecules, and

$$\overline{V}° = 15.8\,\overline{n} + 7.0 \tag{2}$$

for acid anions.

Similar correlations for $\overline{V}°$ of aqueous dicarboxylic acids as well as their monovalent and divalent acid anions are shown in figure 1B. In the

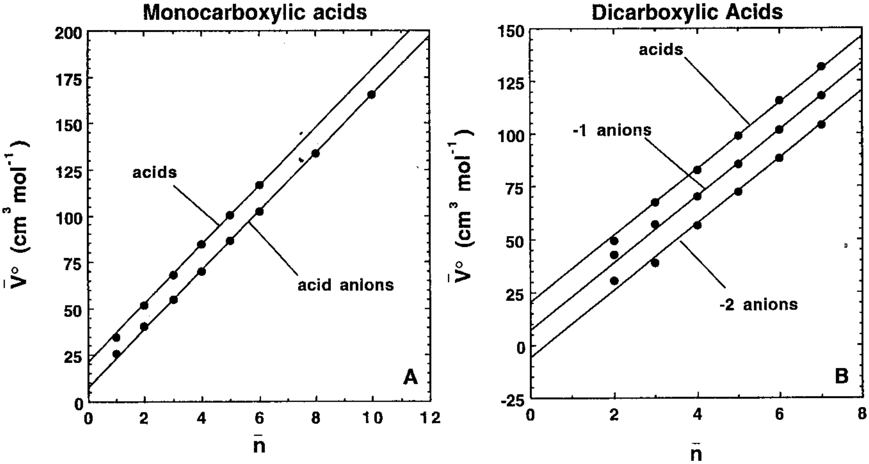


Fig. 1. Standard partial molal volumes of (A) aqueous monocarboxylic acids and monocarboxylate anions and (B) aqueous dicarboxylic acids, as well as monovalent and divalent dicarboxylate anions at 25°C and 1 bar from table 1, plotted against the number of moles of carbon in their stoichiometric formulas ($\overline{n}$). The correlation curves are given by eqs (1) through (5).

case of the aqueous dicarboxylic acid species shown in figure 1B, the correlations are given by

$$\overline{V}^\circ = 15.8\,\overline{n} + 19.6 \tag{3}$$

for the neutral acid molecules,

$$\overline{V}^\circ = 15.8\,\overline{n} + 6.8 \tag{4}$$

for the monovalent anions, and

$$\overline{V}^\circ = 15.8\,\overline{n} - 6.4 \tag{5}$$

for the divalent anions.

Analogous correlations for the more limited $\overline{C}_P^\circ$ data from table 1 are shown in figure 2. The correlations in figure 2A are consistent with

$$\overline{C}_P^\circ = 21.2\,\overline{n} - 2.2 \tag{6}$$

for aqueous neutral monocarboxylic acid species, and

$$\overline{C}_P^\circ = 21.2\,\overline{n} - 37.2 \tag{7}$$

for the acid anions. The slopes of the correlation lines in figure 2A are identical to those for a wide variety of aqueous organic species including n-alkanes, n-alkylbenzenes, primary amines, and primary alcohols, as well as the monocarboxylic acids and acid anions found by Shock and

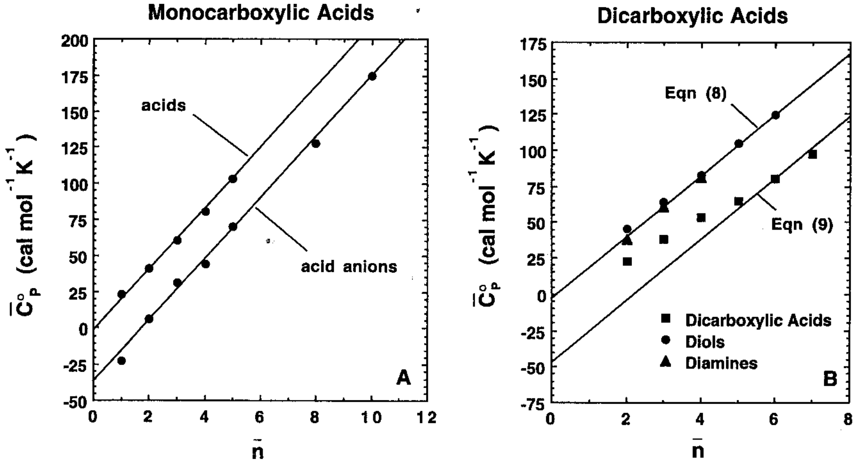


Fig. 2. Standard partial molal isobaric heat capacities at 25°C and 1 bar of (A) aqueous monocarboxylic acids and monocarboxylate anions from table 1 and (B) aqueous diamines, diols and dicarboxylic acids from Nichols and others (1976a), plotted against the number of moles of carbon in their stoichiometric formulas ($\overline{n}$). The correlation curves correspond to eqs (6) through (9).

Helgeson (1990). In each case of homologous groups of monofunctional aqueous organic compounds the slope of the $\overline{C}_P^\circ$ versus $\overline{n}$ plot is 21.2. This is equivalent to saying that the increment in $\overline{C}_P^\circ$ attending the addition of a CH_2 group to an aliphatic aqueous organic compound is 21.2 cal mol^{-1} K^{-1}. This also appears to be the case for difunctional compounds such as diamines and dialcohols (diols) as shown in figure 2B where both homologous groups are consistent with

$$\overline{C}_P^\circ = 21.2\,\overline{n} - 3. \tag{8}$$

It should be noted that these data plotted in figure 2B are for α,ω-diamines and α,ω-diols which are analogous in structure to the dicarboxylic acids considered in the present study. Although the dicarboxylic acids with $\overline{n} \leq 5$ do not fall on the parallel correlation shown in figure 2B and given by

$$\overline{C}_P^\circ = 21.2\,\overline{n} - 47, \tag{9}$$

those with $\overline{n} \leq 6$ do. The distribution of data in figure 2B is consistent with the notion that long-chain dicarboxylic acids ($\overline{n} \leq 6$) will have $\overline{C}_P^\circ$ values consistent with eq (9) and a CH_2 increment consistent with all other aliphatic aqueous organic compounds. It also follows that interactions between the carboxyl groups and surrounding water dipoles are strong enough so that the short-chain dicarboxylic acids have values of $\overline{C}_P^\circ$ which diverge from this trend. Divergence of this type is observed for monofunctional compounds as well (see, for example, formic acid and formate in fig. 2A), but the effect is usually observed for $\overline{n} \leq 2$ or 3.

Direct calorimetric measurements leading to values of $\overline{C}_P^\circ$ for dicarboxylate anions were not found in the present study. Nevertheless, values of $\overline{C}_P^\circ$ can be calculated from heat capacity of dissociation ($\Delta\overline{C}_{P,D}^\circ$) data. As described below, most values of $\Delta\overline{C}_{P,D}^\circ$ come from fits of dissociation constants at elevated temperatures. It was assumed in this study that $\Delta\overline{C}_{P,D}^\circ$ values for malonic acid reported by Kettler, Wesolowski, and Palmer (1992) are good approximations for dicarboxylic acids with $\overline{n} > 3$ as well. These values of $\Delta\overline{C}_{P,D}^\circ$ (see table 3 below) were used to estimate values of $\overline{C}_P^\circ$ for the anions of succinic, glutaric, adipic, and pimelic acid using values of $\overline{C}_P^\circ$ for the acids from table 1. The same values $\Delta\overline{C}_{P,D}^\circ$ were used to evaluate the offset in correlations of the type shown in figure 2B which leads to the following expressions

$$\overline{C}_P^\circ = 21.2\,\overline{n} - 91.0, \tag{10A}$$

and

$$\overline{C}_P^\circ = 21.2\,\overline{n} - 150.8, \tag{10B}$$

which were used in this study to estimate $\overline{C}_P^\circ$ for the mono- and divalent anions of suberic, azelaic and sebacic acid.

Values of $\overline{V}°$ for benzoic acid, benzoate, and *p*-toluate are listed in table 1. The value of $\overline{V}°$ for the *p*-toluate ion was adopted as a close approximation of $\overline{V}°$ for *m*-toluate and *o*-toluate. If it is also assumed that the volume of dissociation ($\Delta\overline{V}^\circ_D$) for toluic acids is the same as that for benzoic acid adopted in this study (-11.7 cm^3 mol^{-1}), $\overline{V}°$ of *p*-toluic acid would be 111.8. This value was adopted in this study and also used for *o*-toluic and *m*-toluic acids. As shown below, values of $\overline{V}°$ for benzoic acid and benzoate from table 1 can be used to predict values of log K for benzoic acid which compare closely with experimental measurements at elevated pressures and temperatures. Similar accuracy is expected for the toluic acids.

Standard partial molal isobaric heat capacities of dissociation ($\Delta\overline{C}^\circ_{P,D}$) of the toluic acids are given by Strong and others (1980) who calculated values of $\Delta\overline{C}^\circ_{P,D}$ from derivatives of their closely spaced measurements of log K from 0° to 100°C. The only experimental value of $\overline{C}^\circ_P$ for the aqueous acid species or the anions is that for *p*-toluate from Perron and Desnoyers (1979) listed in table 1. Using the value of $\Delta\overline{C}^\circ_{P,D}$ for *p*-toluic acid from Strong and others (1980) yields 103.8 cal mol^{-1} K^{-1} for aqueous *p*-toluic acid. As described below, analogies between the toluic acids and the xylenes were used in this study to estimate values of $\overline{S}°$ for the toluic acids. This approach was also used to estimate $\overline{C}^\circ_P$ values for *o*-toluic and *m*-toluic acids. The difference in $\overline{C}^\circ_P$ between *p*-xylene (110.4 cal mol^{-1} K^{-1}) (Shock, 1995) and *p*-toluic acid is -6.6 cal mol^{-1} K^{-1}. If it is assumed that this difference accompanies the removal of a methylene group and its replacement by a carboxyl group, then values of $\overline{C}^\circ_P$ for aqueous *o*-toluic and *m*-toluic acids can be estimated from the values of $\overline{C}^\circ_P$ for the corresponding xylenes from Shock (in preparation) (125.0 and 128.6 cal mol^{-1} K^{-1} for ortho- and meta-xylene, respectively).

$\Delta\overline{G}^\circ_f$, $\Delta\overline{H}^\circ_f$ and $\overline{S}°$.—There is a limited variety of aqueous carboxylic species for which values of the standard partial molal Gibbs free energy of formation ($\Delta\overline{G}^\circ_f$) and standard partial molal entropy ($\overline{S}°$) are available from experimental measurements. These data are compiled in table 2, together with values of the standard partial molal enthalpy of formation ($\Delta\overline{H}^\circ_f$) for which the coverage of neutral monocarboxylic and dicarboxylic acids species is somewhat more inclusive. In contrast to properties of individual carboxylic acid species, there are numerous reports of standard state thermodynamic properties of dissociation reactions at 25°C and 1 bar as summarized in table 3. As in the cases of tables 1 and 2, the first entry in table 3 for each property of an acid corresponds to the value adopted in the present study. Many of the reaction properties at 25°C and 1 bar adopted in the present study were taken from the critical review of Larson and Hepler (1969) who assessed the uncertainty in the experimental data. In a few cases, more recent studies have provided new experimental data and comparisons to earlier results. Notable among these more recent studies are the papers by Strong and coworkers on benzoic and toluic acids and those of Kettler and coworkers on dicarboxylic acids.

TABLE 2

Standard partial molal Gibbs free energies of formation, enthalpies of formation and entropies of aqueous carboxylic acid species at 25°C and 1 bar from experimental measurements

Species	$\Delta\bar{G}^{\circ}_{f}$[a]		$\Delta\bar{H}^{\circ}_{f}$[a]		$\bar{S}^{\circ}$[b]	
formic acid	-88982.[c]	-88860.[j]	-101680.[c]	-101650.[j]	38.9[c]	38.7[j]
acetic acid	-94760.[c]	-94670.[j]	-116100.[c]	-116040.[j]	42.7[c]	42.5[j]
	-96210.[e,s]	-94280.[t]	-115980.[d]			
	-94220.[u]					
propanoic acid			-122470.[d]			
n-butanoic acid			-127950.[d]			
n-pentanoic acid			-133690.[d]			
n-hexanoic acid			-139290.[d]			
n-heptanoic acid			-145080.[d]			
n-octanoic acid			-151050.[d]			
benzoic acid	-56130.[k]	-57950.[e]	-85070.[k]		55.1[k]	
o-toluic acid			-92640.[k]			
m-toluic acid			-95410.[k]			
p-toluic acid			-96190.[k]			
formate	-83862.[f]	-83740.[j]	-101680.[f]	-101630.[j]	21.7[f]	21.6[j]
acetate	-88270.[c]	-88190.[j]	-116160.[h,j]		20.6[g]	20.4[j]
	-89720.[e]					
benzoate	-52250.[e]					
oxalic acid	-168640.[i]		-194860.[h]	-195580.[v]	44.0[l]	
malonic acid			-207870.[m]			
succinic acid	-177800.[j]	-178510.[e]	-218000.[j]	-217930.[v]	62.3[j]	
glutaric acid			-223440.[n]	-221240.[m]		
			-222270.[p]			
adipic acid			-229750.[v]			
pimelic acid			-233720.[q]			
suberic acid			-237760.[r]			
azelaic acid			-240700.[r]			
H-oxalate	-166907.[c]		-195600.[c]		35.7[c]	
H-succinate	-172780.[e]					
oxalate	-161100.[c]		-197200.[c]		10.9[c]	
succinate	-164380.[j]	-165090.[e]	-217350.[j]		19.5[j]	

[a] cal mol^{-1}, [b] cal mol^{-1} K^{-1}, [c] Wagman and others (1982), [d] Calculated from ΔH° of solution (liquid → aqueous) given by Abraham (1984) and ΔH°_{f} of the liquid from Stull, Westrum, and Sinke (1969), [e] Parks and Huffmann (1932), [f] Calculated from data for the acid species accepted in the present study and dissociation properties selected from those listed in table 3 (see text), [g] Shock and Helgeson (1990) from regression of log K data as a function of temperature, [h] Calculated from the accepted values for $\bar{S}^{\circ}$ and $\Delta\bar{G}^{\circ}_{f}$ together with values of S° of the elements from Cox, Wagman, and Medvedev (1989), [i] Calculated from data for the anion accepted in the present study and values of the dissociation reaction selected from those listed in table 3 (see text), [j] Miller and Smith-Magowan (1990), [k] Calculated from hydration reaction (g → aq) property given by Strong, Neff, and Whitesel (1989) together with data for the gas from Stull, Westrum, and Sinke (1969), [l] From regression of the log K data in the present study (see text), [m] Calculated from ΔH°(s → aq) given by Apelblat (1990) and $\Delta\bar{H}^{\circ}_{f}$ of the solid from Domalski (1972), [n] Calculated from ΔH° (s → aq) given by Nichols (1976) and $\Delta\bar{H}^{\circ}_{f}$ of the solid from Domalski (1972), [p] Calculated from ΔH° (s → aq) given by Apelblat and Manzurola (1989) and $\Delta\bar{H}^{\circ}_{f}$ of the solid from Domalski (1972), [q] Calculated from ΔH° (s → aq) given by Apelblat and Manzurola (1989) and $\Delta\bar{H}^{\circ}_{f}$ of the solid from Stull, Westrum, and Sinke (1969), [r] Calculated from ΔH° (s → aq) given by Apelblat and Manzurola (1990) and $\Delta\bar{H}^{\circ}_{f}$ of the solid from Stull, Westrum, and Sinke (1969), [s] Calculated from ΔG° of hydration given by Butler and Ramchandani (1935) together with $\Delta\bar{G}^{\circ}_{f}$ (g) from Wagman and others (1982), [t] Calculated from ΔG° of hydration given by Wolfenden (1976) together with $\Delta\bar{G}^{\circ}_{f}$ (g) from Wagman and others (1982), [u] Calculated from ΔG° of hydration given by Fredenhagen and Liebster (1932), together with $\Delta\bar{G}^{\circ}_{f}$ (g) from Wagman and others (1982), [v] Calculated from ΔH° (s → aq) given by Apelblat (1986), and $\Delta\bar{H}^{\circ}_{f}$ of the solid from Domalski (1972).

Values of $\Delta \overline{H}_f^\circ$ for aqueous monocarboxylic acids from table 2 are shown in figure 3, together with values of $\Delta \overline{H}_f^\circ$ for the corresponding anions calculated as described below. The correlation lines in figure 3 are given by

$$\Delta \overline{H}_f^\circ = -5670.\,\overline{n} - 105500. \tag{11}$$

for the neutral acids, and

$$\Delta \overline{H}_f^\circ = -5670.\,\overline{n} - 106000. \tag{12}$$

for the anions. As in the case of aqueous monocarboxylic acids, values of $\Delta \overline{H}_f^\circ$ are available for several aqueous dicarboxylic acids as listed in table 2. These data are also plotted against $\overline{n}$ in figure 3 where it can be seen that the higher homologues define a correlation corresponding to

$$\Delta \overline{H}_f^\circ = -5670.\,\overline{n} - 192000. \tag{13}$$

The slopes of these correlations are identical to those for many homologous series of aqueous organic compounds found by Shock and Helgeson (1990) including: n-alkanes, n-alkylbenzenes, primary amines, primary alcohols, ketones, methyl alkanoates, and amino acids. These same authors identified correlations involving $\overline{S}^\circ$ for many of the same homologous series and proposed the following expressions which describe the limited data for monocarboxylic acids

$$\overline{S}^\circ = 6.7\,\overline{n} + 29.3, \tag{14}$$

and anions

$$\overline{S}^\circ = 6.7\,\overline{n} + 5.1, \tag{15}$$

respectively. These correlations were adopted in the present study to estimate values of $\overline{S}^\circ$ at 25°C and 1 bar for the many aqueous monocarboxylic acids that have not been studied experimentally. Values of $\overline{S}^\circ$ for neutral aqueous acid species were used together with the $\Delta \overline{H}_f^\circ$ values in table 2 and values of S° for elements from Cox, Wagman, and Medvedev (1989) to calculate values of $\Delta \overline{G}_f^\circ$.

Eqs (14) and (15) are predicated on the assumption that aqueous monocarboxylic acids and their anions behave like other homologous series of aqueous organic compounds (Shock and Helgeson, 1990). In the case of the dicarboxylic acids, values of $\overline{S}^\circ$ are available for only the oxalic and succinic species. It is likely that $\overline{S}^\circ$ values of the oxalic acid species diverge from the trend defined by the higher homologues for reasons mentioned above. Therefore, reliable correlations can not be constructed by considering data for both oxalic and succinic acids. Instead, only the succinic acid data were used to constrain correlations employed in the present study. Values of $\overline{S}^\circ$ for oxalic and succinic acid species from table 2 are shown as solid symbols in figure 4. The lower-most line in this figure

TABLE 3

Standard molal thermodynamic properties of dissociation for aqueous carboxylic acids at 25°C and 1 bar taken from the literature[a]

Acid	ΔG°_{D}[b]	ΔH°_{D}[b]	ΔS°_{D}[c]	$\Delta C^{\circ}_{p,D}$[b]	ΔV°_{D}[d]
formic	5120.[e,aq,cg]	0.[e]	-17.2[e]	-41.[e,aq]	-8.9[cb]
	5123.[dm]	-21.[dm]	-17.4[bq]	-35.[dm]	-9.2[bf]
	5117.[cf]	10.[cj]	-17.3[f,dm]		-8.0[bg]
	5110.[f]	-80.[bq]	-17.1[cj]		-6.0[bt]
	5140.[i]	-40.[f]			-8.5[bu]
	5100.[bx]	-13.[aq]			
	5096.[cj]	-130.[bd]			
		-12.[cy]			
acetic	6480.[e,cj]	-100.[e,f,cy]	-22.1[e,f]	-37.[e]	-11.3[bu]
	6490.[f,m,bb,br,bv,bx,cn,cu,cw,cx]		-21.0[x]	-55.7[x]	-11.2[cb]
	6460.[cm,dh]	-190.[x]	-21.9[db]	-33.9[bl]	-11.6[bf]
	6489.[g]	-70.[bd]			-12.5[bg]
	6495.[h,i]	-98.[by]			-9.2[bh]
	6454.[cg]	-20.[db]			-11.5[bi]
	6500.[x]				-12.1[bj]
	6470.[bm,bv]				-10.6[bt]
					-12.2[bk]
propanoic	6650.[e,f,ap,i,bb,bx]	-160.[e]	-22.9[e]	-33.[e]	-13.0[bu]
	6642.[cj]	-200.[f]	-22.8[db]	-37.7[bl]	-12.0[bt]
	6645.[ar]	-225.[by]	-23.0[f]		-12.9[cb]
	6670.[as]	-80.[bd]			-13.7[bg]
	6634.[ck]	-140.[db]			
		-170.[cy]			
n-butanoic	6580.[e,bb]	-680.[e]	-24.3[e]	-36.[e]	-13.7[bg]
	6575.[f,i]	-640.[f,ch,db]	-24.5[f]	-30.6[u]	
	6550.[bs,cz]	-698.[u]	-24.2[db]		
	6570.[bx]	-730.[bd]			
		-690.[dj]			
		-720.[dl]			
n-pentanoic	6610.[e,af]	-690.[af]	-24.5[e,af]	-33.[e]	
	6606.[bq]	-660.[bq]	-24.4[bq]	-32.[bq]	
	6630.[i]	-720.[e]			
	6645.[bb]				
	6550.[bs]				
n-hexanoic	6630.[e,f,af]	-600.[e]	-24.2[e]	-31.[e]	
	6550.[i,bs]	-670.[f,af]	-24.5[f,af,bq]	-29.8[u]	
	6657.[bq]	-640.[bq]		-33.[bq]	
	6660.[bb]	-644.[u]			
n-heptanoic	6675.[bb,bq]	-610.[af,bq]	-24.3[af]	-33.[bq]	
	6630.[af]		-24.4[bq]		
	6550.[bs]				
n-octanoic	6680.[bb]	-620.[af,bq]	-24.5[af,bq]		
	6670.[af]				
	6677.[bq]				
n-nonanoic	6760.[bb]				
n-dodecanoic	7245.[bz]				
2-methylpropanoic	6620.[f]	-770.[f]	-24.8[e,f]	-31.[e]	-14.9[bu]
	6610.[e]	-780.[e]	-24.7[bq]	-28.8[u]	-13.2[bt]
	6630.[i,bb]	-775.[u]		-36.[bq]	
		-1010.[bd]			
		-750.[bq]			
2-methylbutanoic	6590.[af,bq]	-1240.[af,bq]	-26.1[af,bq]		
3-methylbutanoic	6520.[e,i,bb]	-1190.[e]	-25.9[e]	-30.[e]	
	6523.[af]	-1090.[af]	-25.6[af]	-27.[u]	
	6517.[bq]	-1168.[u]	-25.7[bq]	-23.[bq]	
		-1150.[bq]			
2-methylpentanoic	6563.[af,bq]	-1280.[af,bq]	-26.2[af,bq]	-27.[bq]	
3-methylpentanoic	6610.[e]	-700.[e]	-24.5[af,bq]	-33.[bq]	-17.1[bt]
	6597.[bq]	-1120.[af,bq]	-25.9[af,bq]	-33.[bq]	
	6617.[af]				
4-methylpentanoic	6610.[af,bq]	-620.[af]	-24.3[af]	-28.[bq]	
		-610.[bq]	-24.2[bq]		
2,2-dimethylpropanoic	6870.[af,bv]	-720.[e,af]	-25.5[af]	-33.[bq]	
	6860.[e,bq]	-690.[bq]	-25.4[e]		
	6890.[i,bb]		-25.3[bq]		
2,2-dimethylbutanoic	6877.[af]	-620.[af,bq]	-25.2[af]		
	6730.[bq]		-24.[bq]		

TABLE 3 (*continued*)

Acid	ΔG°_{D}[b]	ΔH°_{D}[b]	ΔS°_{D}[c]	$\Delta C^{\circ}_{p,D}$[b]	ΔV°_{D}[d]
2,2-dimethylpentanoic	6774.[bq]	-990.[bq]	-26.1[bq]	-31.[bq]	
2-ethylbutanoic	6481.[bq]	-1970.[bq]	-28.4[bq]		
benzoic	5730.[e,n,p,ac,bb,bv]	61.[j]	-18.9[e]	-37.[e]	-11.7[x,cb]
	5729.[j]	91.[s]	-19.0[j]	-39.[j]	-11.09[az]
	5726.[k,l]	46.[t]	-18.93[s]	-37.9[s]	-10.6[ba]
	5724.[ay]	110.[u,s]	-19.1[t,cf]	-30.6[t]	
	5749.[m]	105.[v]	-19.4[x]	-47.8[x]	
	5736.[q,x]	150.[db]	-18.7[db]	-35.[u]	
	5737.[az,ct]	118.[w]			
	5755.[de]	-24.[x]			
	5746.[di]	0.0[cf]			
	5722.[cc]	-67.[ac]			
	5700.[cf,cs]	100.[e]			
	5758.[cq]	-90.[d]			
	5712.[cw]				
o-toluic	5317.[y]	-1432.[y]	-22.63[y]	-31.2[y]	
	5330.[e,bb,dd]	-1400.[e,z]	-22.8[e]	-31.[e]	
	5284.[z]	-1022.[aa]	-22.4[z]	-33.1[ab]	
	5300.[aa,ab]	223.[ab]	-21.24[aa]		
		-1500.[ad]	-17.[ab]		
			-22.9[ad]		
m-toluic	5809.[y]	42.[y]	19.34[y]	-41.5[y]	
	5780.[e]	70.[e,z,ad,ae]	19.2[e,z,ad]	-33.[e]	
	5785.[z]	1200.[aa]	15.3[aa]	-142.[ab]	
	5825.[aa]	-204.[ab]	20.1[ab]	-34.[ac]	
	5800.[ab,ac]	-91.[ac]	19.75[ac]		
	5830.[ab,dc]		-19.22[ae]		
p-toluic	5958.[y]	88.[y]	-19.69[y]	-38.3[y]	
	5920.[e,z]	300.[e,z]	-18.9[e,z]	-37.[e]	
	5950.[aa]	1100.[aa]	-16.27[aa]	-354.[ab]	
	5945.[ab]	2242.[ab]	-11.8[ab]	-39.[ac]	
	5960.[ac]	-134.[ac]	-20.24[ac]		
	5970.[dc]	24.[ad]	-19.0[ad]		
phenylacetic	5880.[bb,e,ag]	-880.[e]	-22.7[e]	-25.[e]	-12.73[az]
	5882.[az]				-13.6[cb]
	5877.[ct]				
	5910.[df]				
phenylpropanoic	6360.[bb]				
	6365.[ct]				
oxalic (1)	1743.[r]	-980.[r]	-9.1[r]	-39.[r]	-6.72[be]
	1700.[at,w]	-1020.[e,db]	-8.4[f]		
	1710.[aw,f]	-800.[f]	-9.2[e,db]		
	1730.[e]				
	1620.[bm]				
	1820.[bl]				
	1680.[cr]				
(2)	5835.[r]	-1625.[r]	-25.1[au,r]	-60.5[r]	-11.91[ae]
	5846.[at]	-1659.[u]	-24.8[e]	-57.[e]	
	5650.[at]	-1600.[f]	-24.9[f]		
	5820.[e,au,f]	-1570.[e]	-24.6[db]		
	5886.[cj]	-1500.[db]			
	5870.[cl]				
	5760.[bm]				
	5660.[cr]				
malonic (1)	3890.[e,aj,al]	20.[e]	-13.0[e,bc,dk]	-61.[e]	-10.06[be]
	3891.[dk]	24.[dk]	-12.9[f]	-44.[dk]	
	3880.[f]	40.[f]	-12.0[db]		
	3883.[bc]	290.[db]			
	3950.[ah]	17.[bc]			
	3875.[cj]				
	3940.[bm]				
	3820.[cr,dg]				
	3920.[cg]				
(2)	7773.[dk]	-1226.[dk]	-30.2[dk]	-59.8[dk]	-18.55[be]
	7770.[e,f,bc]	-1150.[e,f]	-29.9[e,f,bc]	-59.[e]	
	7750.[ah]	-1161.[ah]	-30.0[ah]	-58.1[bc]	
	7767.[ai]	-1139.[bc]	-29.2[db]		
	7740.[aj,ak,am]	-920.[db]			
	7720.[al]				

TABLE 3 (*continued*)

Acid	$\Delta G^{\circ b}_{D}$	$\Delta H^{\circ b}_{D}$	$\Delta S^{\circ c}_{D}$	$\Delta C^{\circ b}_{p,D}$	$\Delta V^{\circ d}_{D}$
	7780.[cr]				
	7730.[dg]				
	7760.[cg]				
	7791.[cj]				
	7830.[bm]				
succinic (1)	5740.[e,f,an,bv]	760.[e,an]	-16.7[e,an]	-32.[e]	-12.86[be]
	5720.[ag,bm]	680.[f]	-17.0[f]		
	5743.[cj]	800.[db]	-16.6[db]		
	5730.[cp,dg]				
	5650.[da]				
(2)	7690.[e,f,bp,bv]	40.[e]	-25.7[e]	-52.[e]	-13.58[be]
	7480.[ag]	-40.[f]	-25.9[f]		-13.17[be]
	7670.[bp]	107.[bp]	-26.1[bp]		
	7740.[ca]	60.[db]	-25.6[db]		
	7706.[cj]				
	7700.[dg]				
	7600.[bk]				
glutaric (1)	5920.[e]	-120.[e,db]	-20.3[e,db]	-12.1[ci]	
	5910.[ax]	-100.[ax]	-20.[ax]		
	5660.[ci]	-40.[ci]	-19.1[ci]		
	5870.[da]				
	5895.[dg]				
(2)	7390.[r]	-580.[e,db]	-26.7[e,db]	-12.5[ci]	
	7395.[ax]	-600.[ax]	-27.[ax]		
	7400.[dg]	-770.[ci]	-26.4[ci]		
	7100.[ci]				
	7710.[da]				
adipic (1)	6020.[e]	-300.[e,af,db]	-21.5[e,db]		
	6030.[af,ag,da]		-21.[af]		
	6017.[ce]				
	6025.[cd,dg]				
(2)	7380.[e,ag,ce,da,dg]	-640.[e,db]	-26.9[e,db]		
	7395.[af]	-600.[af]	-27.[af]		
	7406.[cd]				
pimelic (1)	6120.[e,af]	-300.[e,af]	-21.6[e,db]		
	6135.[dg]	-330.[db]	-22.[af]		
	6080.[ca]				
(2)	7400.[e]	-900.[e,af]	-27.9[e,db]		
	7410.[af]	-930.[db]	-28.[af]		
	7405.[dg]				
	7620.[ca]				
suberic (1)	6150.[e]	-390.[e,db]	-21.9[e,db]		
	6160.[dg]				
	6170.[da]				
(2)	7370.[e]	-600.[e]	-26.9[e,db]		
	7390.[dg]	-640.[db]			
	7500.[da]				
azelaic (1)	6170.[bm]				
	6210.[bn,da]				
	6200.[dg]				
(2)	7360.[bm]				
	7390.[bn,dg]				
	7500.[da]				
sebacic (1)	6000.[bw]				
	6280.[da]				
(2)	7120.[aw]				
	7640.[da]				
phthalic (1)	4020.[e]	-640.[e,db]	-15.6[e]	-22.[e]	
	4021.[cj]		-16.[db]		
	4230.[ag]				
(2)	7381.[bj]	-500.[e,db]	-26.4[e]	-70.[e]	
	7370.[ag]		-26.[db]		
	7280.[cm]				
isophthalic (1)	3140.[ag]				
(2)	6360.[ag]				

was drawn through the value for succinate by assuming that the slope of $\overline{S}^{\circ}$ versus $\overline{n}$ would be the same as that for monocarboxylic acids and corresponds to

$$\overline{S}^{\circ} = 6.7\,\overline{n} - 7.3. \tag{16}$$

There is considerable confidence in declaring that the slopes of linear correlations of $\overline{S}^{\circ}$ versus $\overline{n}$ for monovalent anions and neutral aqueous acids will parallel the divalent anion line. This stems from the observation that the $\Delta\overline{S}^{\circ}_{\mathrm{D}}$ values listed in table 3 approach constant values for both dissociations with increasing $\overline{n}$. This is demonstrated in figure 5, where values of $\Delta\overline{S}^{\circ}_{\mathrm{D}}$ from table 2 are plotted. It can be seen that the first dissociation reactions approach $\Delta\overline{S}^{\circ}_{\mathrm{D}} = -21.6$ cal mol^{-1} K^{-1} with increasing $\overline{n}$ and that values of $\Delta\overline{S}^{\circ}_{\mathrm{D}}$ for the second dissociation approach -27.0 cal mol^{-1} K^{-1} with increasing $\overline{n}$. As a consequence, parallel lines are shown in figure 4 for the monovalent anions and neutral acid species. Also shown as open symbols are values of $\overline{S}^{\circ}$ for these species calculated

---

[a] The subscript D refers to the dissociation reaction, [b] cal mol^{-1}, [c] cal mol^{-1} K^{-1}, [d] cm^3 mol^{-1}, [e] Larson and Hepler (1969), [f] Smith and Martell (1989), [g] Harned and Ehlers (1933a), [h] Banerjee, Sen Gupta, and Siddhanta (1958), [i] Lloyd, Wycherley, and Monk (1951), [j] Strong, Kinney, and Fischer (1979), [k] Brockman and Kilpatrick (1934), [l] Saxton and Meier (1934), [m] Dippy and Williams (1934), [n] Smolyakov (1967), [p] Jones and Parton (1952), [q] Travers and others (1975), [r] Kettler, and Palmer, and Wesolowski (1991), [s] Matsui, Ko, and Hepler (1974b), [t] Smolyakov and Primanchuk (1966), [u] Cottrell and others (1948), [v] Fernandez and Hepler (1959), [w] Leung and Gruenwald (1970), [x] Read (1981), [y] Strong and others (1980), [z] Everett and Wynne-Jones (1939), [aa] Wilson and others (1967), [ab] Sengupta and others (1978), [ac] Bolton, Fleming, and Hall (1972), [ad] Zawidski, Papée, and Laidler (1959), [ae] Matsui, Ko, and Hepler (1974a), [af] Martell and Smith (1977), [ag] Topp and Davies (1940), [ah] Nair (1965), [ai] Hamer, Burton, and Acree (1940), [aj] Gelles and Nancollas (1956), [ak] Cannan and Kibrick (1938), [al] Stock and Davies (1949), [am] Davies (1935), [an] Pinching and Bates (1950a), [ap] Harned and Ehlers (1933b), [aq] Harned and Embree (1934a), [ar] Hála and Okác (1962), [as] Muzaffaruddin, Salahuddin, and Malik (1963), [at] Vosburgh and Beckman (1940), [au] Pinching and Bates (1948), [av] Clayton and Vosburgh (1937), [aw] McAuley and Nancollas (1961), [ax] Martell and Smith (1982), [ay] Niazi and others (1990), [az] Fischer, Mann, and Vaughan (1961), [ba] Clark and Ellis (1960), [bb] Dippy (1938), [bc] Das and Ives (1961), [bd] Canady, Papée, and Laidler (1958), [be] Høiland (1975), [bf] Distéche and Distéche (1965), [bg] Hamann and Lim (1954), [bh] Owen and Brinkley (1941), [bi] Redlich and Bigeleisen (1942), [bj] Ellis and Anderson (1961), [bk] Hamann and Strauss (1955), [bl] Edsall (1935), [bm] Simms (1928a,b), [bn] Gane and Ingold (1931), [bp] Pinching and Bates (1950b), [bq] Christensen and others (1970), [br] Bates (1951), [bs] Church and Weiss (1970), [bt] Srivastava and others (1984), [bu] Høiland (1974a), [bv] Wilcox and Leung (1968), [bw] Wenger and Kapétanidis (1960), [bx] Salomon (1986), [by] Olofsson (1984), [bz] Nyrén and Back (1958), [ca] Novikov and others (1966), [cb] Lown, Thirsk, and Wynne-Jones (1968), [cc] Lowe and Smith (1975a), [cd] Litchinsky and others (1969), [ce] Howell and Fisher (1958), [cd] Hermans, Leach, and Scheraga (1963), [cg] Glasoe and Long (1960), [ch] Christensen, Oscarson, and Izatt (1968), [ci] Delben and Crescenzi (1978), [cj] De Robertis and others (1990), [ck] Guilleme and Wojtkowiak (1969a,b), [cl] Parton and Nicholson (1939), [cm] Morton (1928), [cn] MacInnes (1926), [cp] Larsson (1922), [cq] Larsson (1929), [cr] Larsson (1924), [cs] Kolthoff and Bosch (1932), [ct] King and Prue (1961), [cu] Kilpi and Meretoja (1937), [cv] Kilpatrick, Chase, and Riesch (1934), [cw] Ives (1933), [cx] Harned and Ehlers (1932), [cy] Harned and Embree (1934b), [cz] Dondon and Pâris (1961), [da] Dondon (1957a,b), [db] Christensen, Izatt, and Hansen (1967), [dc] Dippy and Lewis (1936), [dd] Dippy and Lewis (1937b), [de] Briscoe and Peake (1938), [df] Bell and Kuhn (1963), [dg] Adell (1940a), [dh] Adell (1940b), [di] Abichandani and Jatkar (1941), [dj] Harned and Sutherland (1934), [dk] Kettler, Wesolowski and Palmer (1992), [dl] Everett, Landsman, and Pinsent (1952), [dm] Bell, Wesolowski and Palmer (1993).

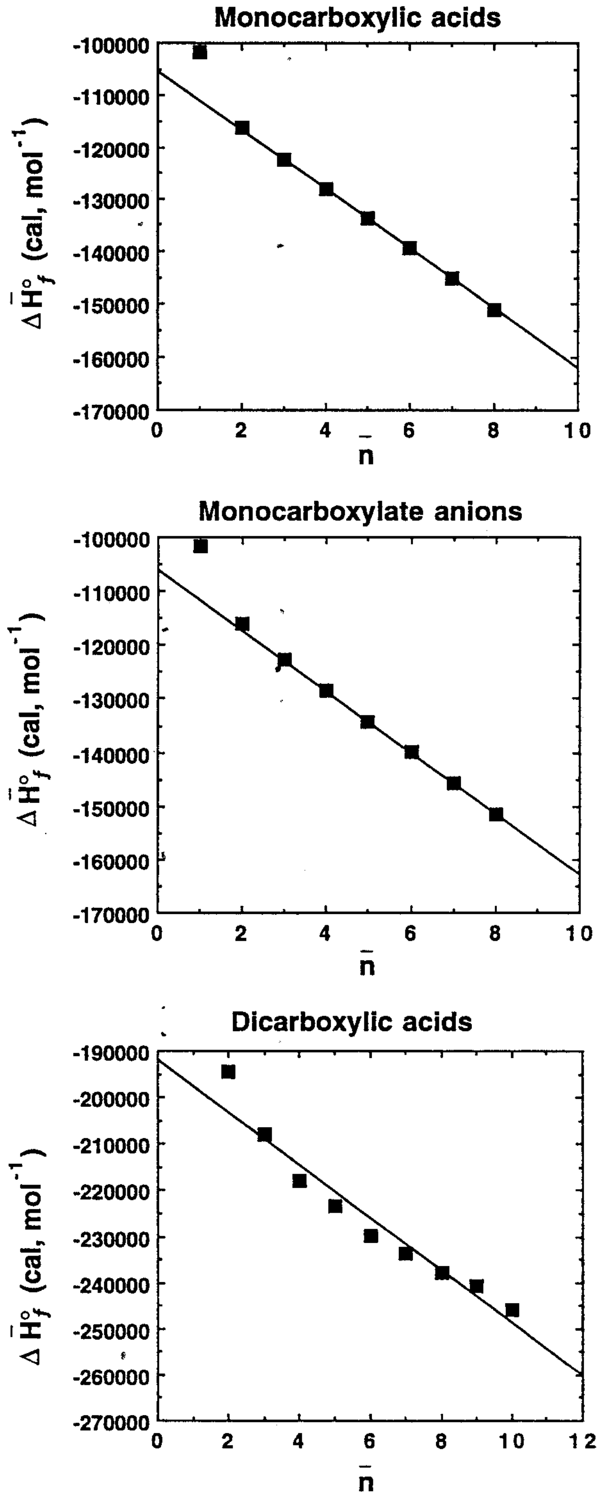


Fig. 3. Standard partial molal enthalpies of formation at 25°C and 1 bar for aqueous (A) monocarboxylic acids, (B) monocarboxylate anions, and (C) dicarboxylic acids from table 2, plotted against the number of moles of carbon in their stoichiometric formulas ($\overline{n}$). The correlation curves are given by eqs (11), (12), and (13).

from values of $\Delta\overline{S}^\circ_D$ taken from table 3 and values of $\overline{S}^\circ$ for divalent anions estimated with eq (16). The offsets between the correlation lines in figure 4 are constrained to equal the constant values of $\Delta\overline{S}^\circ_D$ approached at higher values of $\overline{n}$. The correlation lines are given by

$$\overline{S}^\circ = 6.7\,\overline{n} + 19.7 \tag{17}$$

for monovalent species and

$$\overline{S}^\circ = 6.7\,\overline{n} + 41.3 \tag{18}$$

for neutral acid species. It is therefore required that the predicted correlation lines are closely consistent with the calculated values of $\overline{S}^\circ$ for the higher homologues of the dicarboxylic acids species as shown in figure 4.

Values of $\overline{S}^\circ$ estimated with eq (18) together with values of $\Delta\overline{H}^\circ_f$ for neutral acid species from table 2 and/or estimated with eq (15) were used to calculate $\Delta\overline{G}^\circ_f$ for the neutral acid species. These values were combined with selected values of $\Delta\overline{G}^\circ_D$ for the two dissociation reactions from table 3 to evaluate $\Delta\overline{G}^\circ_f$ for the acid anions. In the case of sebacic acid, values of 6200 cal mol^{-1} and 7400 cal mol^{-1} for the first and second dissociation reactions were estimated in this study based on data for the other higher

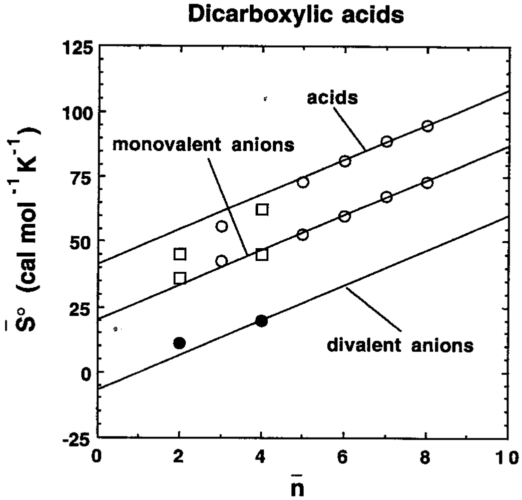


Fig. 4. Standard partial molal entropies of aqueous dicarboxylic acids and dicarboxylate anions at 25°C and 1 bar plotted against the number of moles of carbon in their stoichiometric fomulas ($\overline{n}$). The solid symbols for oxalate and succinate represent data taken from table 2, the open circles represent values of $\overline{S}^\circ$ calculated from the values of $\Delta\overline{S}^\circ_D$ from table 3 and values of $\overline{S}^\circ$ for divalent anions estimated with eq (16). Open squares represent values calculated with $\Delta\overline{S}^\circ_D$ values from table 3 and $\overline{S}^\circ$ for divalent anions shown in the figure. Correlation curves are given by eqs (16), (17), and (18).

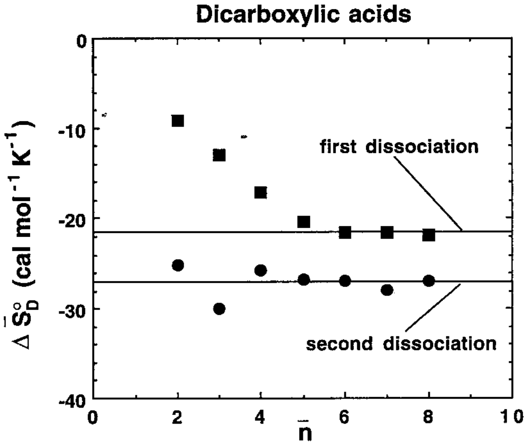


Fig. 5. Standard partial molal entropies of dissociation of aqueous dicarboxylic acids at 25°C and 1 bar from table 3, plotted against the number of moles of carbon in their structural formulas ($\bar{n}$). Horizontal lines correspond to limiting values exhibited by the higher homologues (see text).

homologues. Values of $\Delta \bar{G}^\circ_f$ for anions from table 2 or calculated as described above were combined with values of $\bar{S}^\circ$ estimated with eqs (16) and (17) and values of S° of the elements from Cox, Wagman, and Medvedev (1989) to calculate the values of $\Delta \bar{H}^\circ_f$ for monovalent and divalent anions.

Thermodynamic data for some aromatic acids are given in tables 1, 2, and 3. The most complete set of data is for benzoic acid. Although Strong, Neff, and Whitesel (1989) evaluate $\Delta \bar{G}^\circ$, $\Delta \bar{H}^\circ$, and $\Delta \bar{S}^\circ$ for solid solubility and gas hydration reactions of toluic acids, only values of ΔH°_f of the solids are available from experiments (Stull, Westrum, and Sinke, 1969). Therefore, other means of obtaining values of $\bar{S}^\circ$ and $\Delta \bar{G}^\circ_f$ for the aqueous toluic acids were sought in the present study. Values of $\bar{S}^\circ$ for the neutral toluic acid species were estimated from the properties of aqueous xylenes given by Shock (1995) after making the following observations. First, the difference between intercepts of $\bar{S}^\circ$ versus $\bar{n}$ correlations for alkanes (intercept = 12.8 cal mol^{-1} K^{-1}, Shock and Helgeson, 1990) and carboxylic acids (eq 14) is 16.5 cal mol^{-1} K^{-1}. This value can be used to estimate $\bar{S}^\circ$ for benzoic acid from the corresponding correlation of $\bar{S}^\circ$ versus $\bar{n}$ for alkylbenzenes

$$\bar{S}^\circ = 6.7\,\bar{n} + 36.3 \tag{19}$$

given by Shock and Helgeson (1990)[21] by adding 16.5 to the intercept to

---

[21] Note that the intercept for alkylbenzenes listed in table 5 of Shock and Helgeson (1990) is in error and should be 36.3.

yield

$$\bar{S}^\circ = 6.7\,\bar{n} + 52.8. \tag{20}$$

In the case of alkylbenzenes, $\bar{n}$ corresponds to the number of carbons in the alkyl chain attached to the benzene ring. As a consequence, $\bar{n}$ for benzene equals zero, and $\bar{n}$ for benzoic acid should also equal zero. Therefore, eq (20) yields an estimate of 52.8 cal mol^{-1} K^{-1} for $\bar{S}^\circ$ of aqueous benzoic acid which is similar to the value obtained experimentally by Strong, Neff, and Whitesel, (1989) (55.1 cal mol^{-1} K^{-1}) listed in table 2. This close agreement supports the usefulness of this type of estimation procedure for phenylcarboxylic acids. However, it does not permit accounting for other substitutions around the benzene ring.

The second assumption is based on the observation that the three toluic acids differ from benzoic acid in that a methyl group is present in the ortho-, meta-, or para-positions. Therefore, these acids can be considered to be the three possible carboxylic acid forms of toluene, which reveals the origin of their name. Alternatively, the differences in the standard partial molal properties of benzoic acid and toluene can be considered to stem from the combined effects of replacing the methyl group in toluene with the carboxyl group in benzoic acid. In the case of $\bar{S}^\circ$, the difference between the corresponding properties of aqueous toluene and benzoic acid is 10.6 cal mol^{-1} K^{-1} which is closely consistent with the difference between values estimated with eqs (19) and (20). It was assumed in this study that the same value would characterize the differences in $\bar{S}^\circ$ between the three toluic acids and the three aqueous xylenes, which are the three possible dimethyl benzene compounds. Values of $\bar{S}^\circ$ for ortho-, meta-, and para-xylene (47.3, 48.7, and 47.7, cal mol^{-1} K^{-1}, respectively) were adopted from the regression of solubility data reported by Shock (in preparation). These values and the assumptions outlined above permit estimation of $\bar{S}^\circ$ values for the toluic acids corresponding to 57.9, 59.3, and 58.3 cal mol^{-1} K^{-1} for ortho-, meta-, and para-toluic acids respectively. These values, together with values of $\Delta \bar{H}_f^\circ$ from table 2, allow calculation of $\Delta \bar{G}_f^\circ$ for these acids, which can be combined with dissociation reaction data from table 3 to evaluate the corresponding properties of the anions. Values of $\Delta \bar{G}_f^\circ$, $\Delta \bar{H}_f^\circ$, and $\bar{S}^\circ$, as well as values of $\bar{V}^\circ$ and $\bar{C}_P^\circ$ adopted in this study for aqueous monocarboxylic, dicarboxylic, and aromatic acids, are listed in table 4, together with values of equation of state parameters obtained as described in the next section.

RETRIEVAL AND ESTIMATION OF EQUATION OF STATE PARAMETERS

Once experimental measurements on aqueous solutions of carboxylic acids and carboxylate salts have been extrapolated to the standard state (see app. 1), the data can be regressed for equation of state parameters with appropriate expressions of the revised-HKF equation of state. Accurate evaluation of conventional and effective Born coefficients (ω and ω_e, respectively) from experiments is only possible through

TABLE 4

Summary of standard partial molal thermodynamic data at 25°C and 1 bar for aqueous carboxylic acid species adopted in this study, together with equation of state parameters required to calculate the corresponding properties at high temperatures and pressure. Unless otherwise indicated, thermodynamic data in this table correspond to selected values in tables 1 and 2, and parameters were estimated with the revised correlation algorithm

Species	$\Delta\bar{G}_f^{\circ}$[a]	$\Delta\bar{H}_f^{\circ}$[a]	$\bar{S}^{\circ}$[b]	$\bar{C}_P^{\circ}$[b]	$\bar{V}^{\circ}$[c]	$a_1^d \times 10^{-2}$	$a_2^d \times 10^{-2}$	a_3^e	$a_4^f \times 10^{-4}$	c_1^b	$c_2^f \times 10^{-4}$	$\omega_e^a \times 10^{-5}$
formic acid	-88982.	-101680.	38.9	22.8	34.69	6.3957	7.7713	2.8318	-3.1002	26.1[ar]	3.1[ar]	-0.33[ar]
acetic acid	-94760.	-116100.	42.7	40.56	52.01	11.6198	5.2180	2.5088	-2.9946	42.076[ar]	-1.5417[ar]	-0.15[ar]
propanoic acid	-93450.[j]	-122470.	49.4[i]	60.5	67.9	11.0057	18.7077	-0.7792	-3.5523	62.97[ar]	-1.19[ar]	-0.15[ar]
butanoic acid	-91210.[j]	-127950.	56.1[i]	80.5	84.61	13.2702	23.3487	-0.6985	-3.7441	72.4342	2.9924	-0.2155
pentanoic acid	-89240.[j]	-133690.	62.8[i]	103.3	100.5	15.4596	28.3156	-1.8374	-3.9495	91.0659	5.2450	-0.1710
hexanoic acid	-87120.[j]	-139290.	69.5[i]	125.0[h]	116.55	17.6709	33.3251	-2.9700	-4.1566	108.8183	7.3890	-0.1266
heptanoic acid	-85200.[j]	-145080.	76.2[i]	146.2[h]	131.6[g]	19.7454	38.0251	-4.0341	-4.3509	126.1711	9.4836	-0.0822
octanoic acid	-83450.[j]	-151050.	82.9[i]	167.4[h]	147.4[g]	21.9224	42.9621	-5.1613	-4.5550	143.5241	11.5781	-0.0378
nonanoic acid	-81220.[j]	-156530.[k]	89.6[i]	188.6[h]	163.2[g]	24.0995	47.8926	-6.2728	-4.7588	160.8768	13.6727	0.0066
decanoic acid	-79170.[j]	-162200.[k]	96.3[i]	209.8[h]	179.0[g]	26.2766	52.8294	-7.4002	-4.9629	178.2298	15.7672	0.0510
undecanoic acid	-77130.[j]	-167870.[k]	103.0[i]	231.0[h]	194.8[g]	28.4537	57.7661	-8.5272	-5.1670	195.5826	17.8618	0.0955
dodecanoic acid	-75080.[j]	-173540.[k]	109.7[i]	252.2[h]	210.6[g]	30.6308	62.6966	-9.6387	-5.3708	212.9354	19.9564	0.1399
benzoic acid	-56130.[j]	-85070.	55.1	89.0	98.77	15.2056	27.7392	-1.7049	-3.9256	79.1665	3.8322	-0.2221
o-toluic acid	-54770.[j]	-92640.	57.9[l]	118.4[l]	111.8[ad]	16.9949	31.7947	-2.6262	-4.0933	102.8349	6.7369	-0.2035
m-toluic acid	-57960.[j]	-95450.	59.3[l]	122.0[l]	111.8[ad]	16.9981	31.7988	-2.6205	-4.0935	105.7976	7.0926	-0.1942
p-toluic acid	-58440.[j]	-96190.	58.3[l]	103.8[ap]	111.8[ad]	16.9958	31.7924	-2.6157	-4.0932	91.1907	5.2944	-0.2009
oxalic acid	-168640.[j]	-194580.	44.0	22.7	49.43	8.4291	12.3793	1.7866	-3.2907	25.4994	-2.7181	-0.2957
malonic acid	-175420.[j]	-207870.	55.7[p]	38.4	66.82	10.8349	17.8340	0.5436	-3.5162	38.7620	-1.1670	-0.2181
succinic acid	-177800.	-218000.	62.3	53.3	82.44	12.9872	22.7109	-0.5623	-3.7178	51.0740	0.3050	-0.1744
glutaric acid	-176780.[j]	-223440.	73.2[p]	64.1	98.98	15.2749	27.8946	-1.7361	-3.9321	60.3712	1.3721	-0.1021
adipic acid	-172790.[j]	-229750.	81.3[p]	80.1	115.15	17.5058	32.9525	-2.8895	-4.1412	73.6536	2.9529	-0.0484
pimelic acid	-172380.[j]	-253720.	89.1[p]	98.0	131.93	19.8194	38.1932	-4.0727	-4.3578	88.4361	4.7214	0.0033
suberic acid	-168490.[j]	-237760.	95.1[p]	122.6[n]	146.0[m]	21.7582	42.5872	-5.0703	-4.5395	108.4636	7.1519	0.0431
azelaic acid	-163660.[j]	-240700.	101.6[ah]	143.8[n]	161.8[m]	23.9348	47.5253	-6.2031	-4.7436	125.8045	9.2464	0.0862
sebacic acid	-161240.[j]	-246000.[q]	108.3[ah]	165.[n]	177.6[m]	26.1119	52.4558	-7.3146	-4.9474	143.1573	11.3410	0.1306
formate	-83862.	-101680.	21.7	-22.0	26.16	5.7842	4.7242	7.3630	-2.9742	17.0[r]	-12.4[r]	1.3003
acetate	-88270.	-116160.	20.6	6.2	40.5	7.7525	8.6996	7.5825	-3.1385	26.3[r]	-3.86[r]	1.3182
propanoate	-86780.[j]	-122630.[x]	26.5[s]	30.9	54.95	9.6992	12.1344	9.0612	-3.2805	52.3[r]	-4.2[r]	1.2276
butanoate	-84650.[j]	-128630.[x]	31.8[s]	44.5	70.3	11.7724	17.0492	7.4458	-3.4837	62.3135	-3.5666	1.1469
pentanoate	-82630.[y]	-134380.[ab]	38.3[s]	70.3	86.31	13.9304	24.8456	-1.0403	-3.8060	86.5816	-3.2539	1.0496
hexanoate	-80490.[y]	-139870.[ab]	45.3[s]	90.0[u]	102.21	16.0700	29.6995	-2.1530	-4.0067	104.8115	-3.0151	0.9427
heptanoate	-78525.[y]	-145620.[ab]	52.0[t]	111.2[u]	116.91	18.0474	33.1726	-0.6108	-4.1503	124.5591	-2.7582	0.8417
octanoate	-76770.[y]	-151580.[ab]	58.7[t]	128.0	133.82	20.3271	39.3469	-4.3421	-4.4055	140.0102	-2.5545	0.7402
nonanoate	-74770.[y]	-156990.[ab]	65.4[t]	153.6[u]	149.2[v]	22.3974	44.0392	-5.4082	-4.5995	164.0445	-2.2443	0.6387
decanoate	-72460.[j]	-162700.[w]	72.1[t]	175.0	165.19	24.5511	48.6514	-5.8334	-4.7901	181.64[ar]	-1.81[ar]	0.5372

undecanoate	-70410.[j]	-168370.[w]	78.8[t]	196.0[u]	180.8[v]	26.6529	53.6845	-7.5999	-4.9982	203.5298	-1.7304	0.4356
dodencanoate	-68370.[j]	-174040.[w]	85.5[t]	210.8	196.1	28.7122	58.3495	-8.6541	-5.1911	217.0287	-1.5510	0.3340
benzoate	-50400.[y]	-84990.[ab]	36.2[s]	51.41	87.03	14.0396	25.0153	-0.8986	-3.8130	68.4490	-3.4828	1.0813
o-toluate	-49440.[y]	-94070.[ab]	35.1[s]	87.4[ac]	100.12[l]	15.8364	29.1695	-2.0312	-3.9848	103.7040	-3.0466	1.0977
m-toluate	-52150.[y]	-95350.[ab]	39.9[s]	80.5[ac]	100.12[l]	15.8115	29.1099	-2.0100	-3.9823	96.2963	-3.1302	1.0242
p-toluate	-52480.[y]	-96160.[ab]	38.3[aq]	65.5	100.12	15.8201	29.1311	-2.0189	-3.9832	81.8997	-3.3120	1.0496
H-oxalate⁻	-166907.	-195600.	36.0[af]	-16.3	42.36	7.9276	11.2406	2.0500	-3.2436	6.5915[an]	-6.3548[am]	1.0831
H-malonate⁻	-171530.[y]	-207850.[ab]	42.7[af]	-5.6[as]	57.07	9.9065	15.7293	1.0227	-3.4291	11.9343	-4.1738	0.9826
H-succinate⁻	-172060.[y]	-217350.[ab]	45.2[af]	9.3[as]	69.99	11.6617	19.7057	0.1226	-3.5935	26.1173	-3.9932	0.9446
H-glutarate⁻	-170860.[y]	-223570.[ab]	52.9[af]	20.1[as]	85.88	13.7966	24.5470	-0.9823	-3.7937	35.5763	-3.8623	0.8279
H-adipate⁻	-166770.[y]	-227130.[ab]	59.8[af]	36.1[as]	102.09	15.9795	29.4936	-2.1047	-3.9982	50.2189	-3.6684	0.7234
H-pimelate⁻	-166260.[y]	-234040.[ab]	67.5[af]	54.[as]	117.7	18.0762	34.2416	-3.1742	-4.1944	66.6044	-3.4514	0.6069
H-suberate⁻	-162340.[y]	-238130.[ab]	73.2[af]	78.6[ai]	133.2[ak]	20.1680	38.9836	-4.2530	-4.3905	89.8033	-3.1533	0.5205
H-azelate⁻	-157490.[y]	-240970.[ab]	80.0[ag]	99.8[ai]	149.0[ak]	22.2952	43.8077	-5.3553	-4.5899	109.5312	-2.8963	0.4174
H-sebacate⁻	-155040.[aa]	-246230.[ab]	86.7[ag]	121.0[ai]	164.8[ak]	24.4230	48.6302	-6.4512	-4.7893	129.2733	-2.6394	0.3158
oxalate⁻²	-161100.	-197200.	10.9	-73.3	30.30	6.9414	9.6716	0.8669	-3.1787	-10.7618[an]	-18.6787[am]	3.0480
malonate⁻²	-163760.[z]	-209000.[ab]	12.8[ae]	-65.4[as]	38.43	8.0442	11.5030	1.9943	-3.2544	-27.6299	-4.8985	3.0192
succinate⁻²	-164380.	-217350.	19.5	-50.5[as]	56.32	10.4577	15.8622	3.5716	-3.4346	-14.0383	-4.7180	2.9170
glutarate⁻²	-163470.[z]	-224140.[ab]	26.2[ae]	-39.7[as]	72.20	12.5965	21.8248	-0.3592	-3.6811	-4.4360	-4.5871	2.8159
adipate⁻²	-159390.[z]	-227780.[ab]	32.9[ae]	-23.7[as]	88.46	14.7868	26.7894	-1.4877	-3.8864	10.2229	-4.3931	2.7131
pimelate⁻²	-158860.[z]	-234960.[ab]	39.6[ae]	-5.8[as]	104.06	16.8882	31.5501	-2.5641	-4.0832	26.7751	-4.1762	2.6147
suberate⁻²	-154970.[z]	-238780.[ab]	46.3[ae]	18.8[aj]	119.83	19.0114	36.3659	-3.6667	-4.2823	49.8209	-3.8780	2.5118
azelate⁻²	-150130.[z]	-241660.[ab]	53.0[ae]	40.0[aj]	135.8[al]	21.1627	41.2392	-4.7685	-4.4837	69.5701	-3.6211	2.4110
sebacate⁻²	-147640.[aa]	-246880.[ab]	59.7[ae]	61.2[aj]	151.13	23.2262	45.9181	-5.8361	-4.6772	89.3135	-3.3642	2.3095

[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] estimated with eq (1), [h] estimated with eq (6), [i] estimated with eq (13), [j] calculated from $\Delta\overline{H}_f^\circ$ and $\overline{S}^\circ$ in table together with values of S° of the elements from Cox, Wagman and Medvedev (1989), [k] estimated with eq (11), [l] estimated as described in text, [m] estimated with eq (3), [n] estimated with eq (9), [p] estimated with eq (16), [q] estimated with eq (13), [r] Shock and Helgeson (1990), [s] Calculated from $\overline{S}^\circ$ for the acid in the table and selected values of $\Delta\overline{S}_D^\circ$ from table 3, [t] estimated with eq (15), [u] estimated with eq (7), [v] estimated with eq (2), [w] estimated with eq (12), [x] calculated from $\Delta\overline{H}_f^\circ$ for the acid in the table and selected value of $\Delta\overline{H}_D^\circ$ from table 3, [y] Calculated from $\Delta\overline{G}_f^\circ$ in the table for the undissociated aqueous acid, together with $\Delta\overline{G}_{D,1}^\circ$, from table 3, [z] Calculated from $\Delta\overline{G}_f^\circ$ in the table for the monovalent anion, together with $\Delta\overline{G}_{D,2}^\circ$ from table 3, [aa] Calculated from $\Delta\overline{G}_f^\circ$ in the table for the undissociated aqueous acid and values of $\Delta\overline{G}_{D,1}^\circ = 6200.$ and $\Delta\overline{G}_{D,2}^\circ = 7400.$ estimated in the present study (see text), [ab] Calculated from $\Delta\overline{G}_f^\circ$ and $\overline{S}^\circ$ in the table, together with S° for the elements from Cox, Wagman and Medvedev (1989), [ac] Calculated from $\overline{C}_P^\circ$ for the acid in the table and selected value of $\Delta\overline{C}_{P,D}^\circ$ from table 3, [ad] Calculated from $\overline{V}^\circ$ of the anion in the table and estimated value of $\overline{V}_D^\circ$ (see text), [ae] Estimated with eq (16), [af] Calculated from the value of $\overline{S}^\circ$ for the corresponding divalent anion together with the value of $\Delta\overline{S}_D^\circ$ in table 3, [ag] Estimated with eq (17), [ah] Estimated with eq (18), [ai] Estimated with eq (10A), [aj] Estimated with eq (10B), [ak] Estimated with eq (4), [al] Estimated with eq (5), [am] estimated with eq (27) (see text), [an] Calculated with eq (A-6) together with values of $\overline{C}_P^\circ$ and other equation of state parameters from the table, [ap] Calculated from $\overline{C}_P^\circ$ for the corresponding anion in the table and selected value of $\Delta\overline{C}_{P,D}^\circ$ from table 3, [aq] Evaluated through regression of log K data, [ar] From table 6, [as] Estimated by assuming $\Delta\overline{C}_{P,D}^\circ$ for this acid is the same as that for malonic acid.

regression of standard state data obtained at temperatures $>150°C$ (Shock, Helgeson, and Sverjensky, 1989). The available data for aqueous carboxylic acids and carboxylate salts at these temperatures are severely limited, requiring estimation of values of the conventional and effective Born coefficients for many species of interest. In the present study, estimation procedures outlined by Shock and Helgeson (1988) for aqueous anions and Shock (1995) for neutral aqueous organic compounds were used. In the case of carboxylate anions, values of ω were calculated with eqs (A-26) and (A-27) in app. 1, with values of $r_{e,j}$ estimated from the standard partial molal entropies of the ions at 25°C and 1 bar, and the relation

$$r_{e,j} = \frac{z_j^2(\eta Y - 100)}{\bar{S}° - \alpha_z} \tag{21}$$

where α_z is equal to 72 for monovalent and 141 for divalent anions (Shock and Helgeson, 1988). Values of ω_e for HCOOH, CH_3COOH, and C_2H_5COOH were obtained through simultaneous regression of equilibrium dissociation constants at temperatures up to 350°C and calorimetric and volumetric measurements up to $\sim 130°C$. Values of ω_e for the remainder of the neutral aqueous carboxylic acid species were estimated from values of $\bar{S}°$ and the relation

$$\omega_e = 661.98\,\bar{S}° - 58740. \tag{22}$$

which is obtained from correlations described by Shock (1995) involving aqueous hydrocarbons and carboxylic acids.

Values of ω and ω_e allow calculation of the solvation contributions to the standard partial molal volumes ($\Delta\bar{V}_s^\circ$) and heat capacities ($\Delta\bar{C}_{P,s}^\circ$) of aqueous organic compounds and electrolytes composed of organic anions. Values of $\Delta\bar{V}_s^\circ$ calculated with eqs (A-10) and (A-17) can be combined with values of $\bar{V}^\circ$ to evaluate $\Delta\bar{V}_n^\circ$ with the first identity of eq (A-5). In cases where data are collected at several temperatures, a plot of $\Delta\bar{V}_n^\circ$ against $1/(T - \theta)$ yields values of σ and ξ (see eq A-11). Although few investigators have measured $\bar{V}^\circ$ values at temperatures other than 25°C for aqueous carboxylic acids and carboxylate electrolytes, several sets of data were regressed with this procedure to obtain values of σ and ξ in this study. Values of σ and ξ for the anions were obtained by subtracting the corresponding values for Na^+ taken from Shock and Helgeson (1988) from the results for the electrolytes. These values are listed in table 5, and the regression plots from which these values were obtained are shown in figure 6.

Standard partial molal heat capacity data for solutions of the sodium salts of formate, acetate, and propanoate were regressed in an analogous manner by Shock and Helgeson (1990), and those results were adopted in this study. In the regression of $\bar{C}_P^\circ$ data, values of $\Delta\bar{C}_{P,s}^\circ$ obtained with eqs (A-14) and/or (A-18) allow evaluation of $\Delta\bar{C}_{P,n}^\circ$ which can in turn be

TABLE 5

Volumetric data at 25°C and 1 bar for aqueous carboxylic acids and acid anions, together with equation of state parameters obtained by regression

Species	$\bar{V}^{\circ a}$	$\Delta\bar{V}_n^{\circ a}$	σ^a	$\xi^b \times 10^{-2}$
acetic acid	52.01	51.64	57.01	−3.72
propanoic acid	67.9	67.53	76.14	−5.58
formate	26.16	29.37	31.80	−1.83
acetate	40.5[c]	44.0[c]	46.43[c]	−1.83[c]
propanoate	54.95	57.98	60.10	−1.80
butanoate	70.3	73.1	76.68	−3.10
heptanoate	116.91	118.99	128.87	−6.46
decanoate	165.19	166.51	180.98	−9.72
benzoate	87.03	89.7	98.98	−6.32
oxalate	30.30	37.82	44.60	−4.80
succinate	56.32	63.52	69.27	−4.12

[a] $cm^3\ mol^{-1}$, [b] $cm^3\ K\ mol^{-1}$, [c] Shock and Helgeson (1990).

regressed with eq (A-16) to obtain values of c_1 and c_2. Constraints on the appropriate value of ω_e for formic, acetic, and propanoic acids come from the temperature dependence of $\bar{C}_P^{\circ}$ data and from regression of high temperature dissociation constants. Regression results can be depicted graphically by plotting $\Delta\bar{C}_{P,n}^{\circ}$ versus $1/(T - \theta)^2$, which is done in figure 7 for Na-decanoate, formic acid, acetic acid, and propanoic acid. The heat capacity data for Na-decanoate reported by DeLisi, Perron, and Desnoyers (1980), which were regressed in the present study, are shown in figure 7 and can be compared with data reported by Choudhury and Ahluwalia (1982a) which they calculated from finite differences of heat of solution measurements. The considerable uncertainty which can be encountered in this approach precluded regression of the latter data in this study. Heat capacity measurements for propanoic acid reported by Makhatadze and Privalov (1990) shown in figure 7 were regressed in this study to obtain the parameters listed in table 6. Note that these data are on average about 5 cal $mol^{-1}\ K^{-1}$ more positive than the values reported by Ackermann and Schreiner (1958). By analogy to the propanoic acid results, the trend of the data reported by Ackermann and Schreiner (1958) for formic acid was used to evaluate the c_2 parameter (solid line in fig. 7), but the c_1 parameter was adjusted (dashed line) to represent the $\bar{C}_P^{\circ}$ value at 25°C reported by Konicek and Wadsö (1971). All values of c_1, c_2, ω, and/or ω_e obtained by regression of data for carboxylic species are listed in table 6.

In the absence of experimental data covering a range of temperatures, species-dependent equation of state parameters for ions as well as neutral acid molecules can be estimated from correlations. Values of σ and $\Delta\bar{V}_n^{\circ}$ from table 5 are plotted in figure 8 together with corresponding values for aqueous inorganic ions from Shock and Helgeson (1988), dissolved gases and boric acid from Shock, Helgeson, and Sverjensky (1989), and aqueous hydrocarbons from Shock (in preparation). It can be

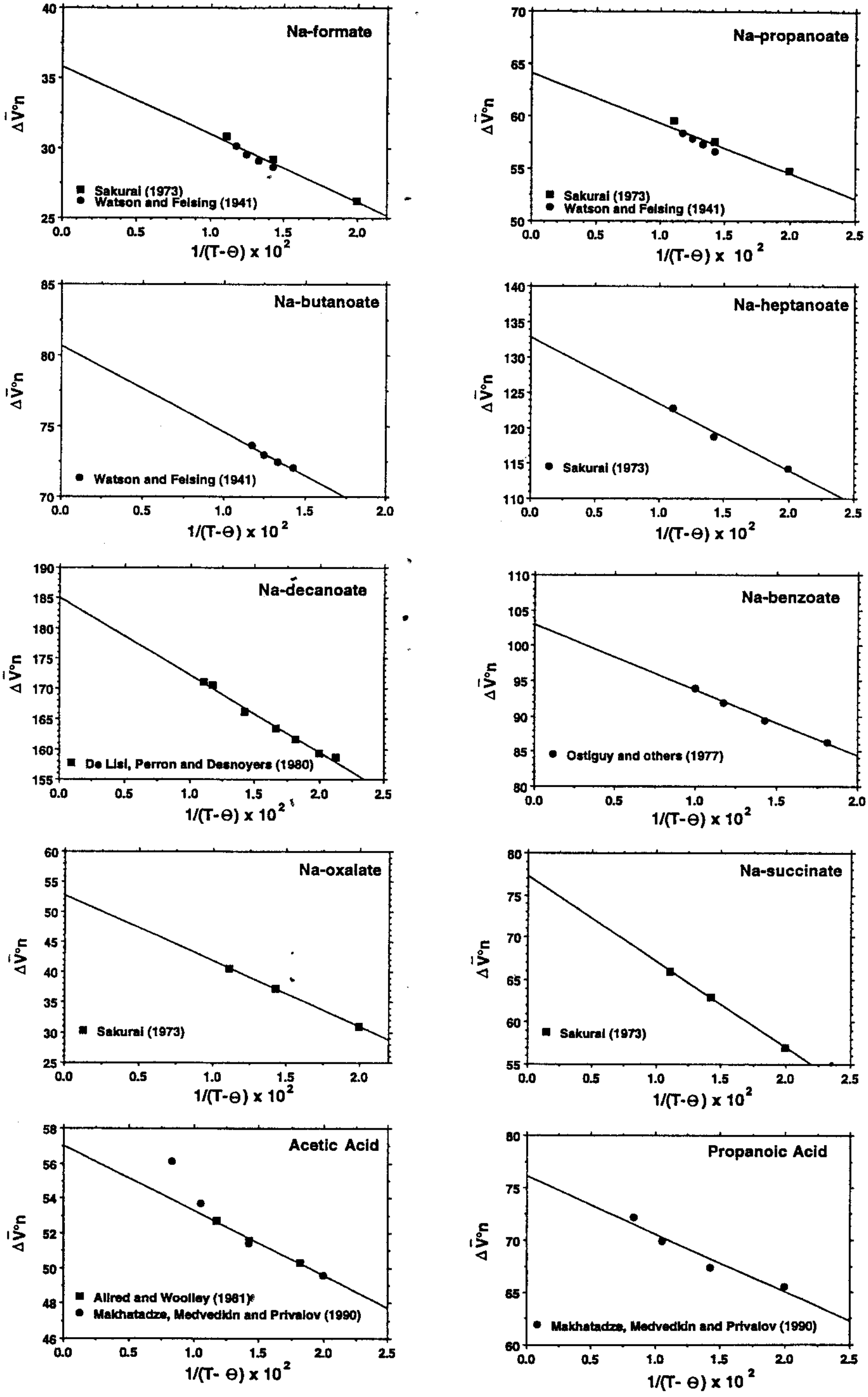


Fig. 6. Regression plots of $\Delta\overline{V}^{\circ}_{n}$ against $1/(T - \theta)$ for acetic acid, propanoic acid, and various Na-carboxylate electrolyetes. Symbols represent experimental data, and the lines indicate the result of regression of the data with eq (A-11).

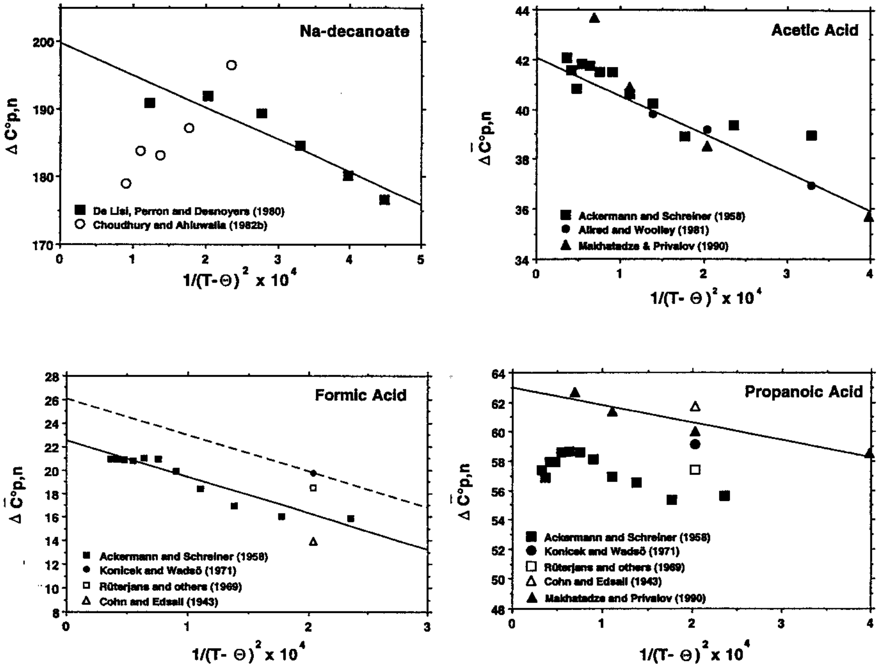


Fig. 7. Regression plot of $\Delta\bar{C}^{\circ}_{P,n}$ against $1/(T-\theta)^2$ for Na-decanoate, formic acid, acetic acid, and propanoic acid. Symbols represent experimental data, and the lines indicate the results of regression of the data with eq (A-16). See text for discussion of differences among experimental data and the details of the regression procedure.

TABLE 6

Standard partial molal heat capacities at 25°C and 1 bar and values of the c_1, c_2, and ω_e equation of state parameters obtained from regression of experimental data in the present study unless otherwise indicated.

Species	$\bar{C}_p^{\circ\,a}$	c_1^a	$c_2^b \times 10^{-4}$	$\omega_e^c \times 10^{-5}$
formic	22.8	26.1	−3.1	−0.33
acetic	40.56	42.076	−1.5417	−0.15
propanoic	60.5	62.97	−1.19	−0.15
formate	−22.0[d]	17.0[d]	−12.4[d]	1.3003[d]
acetate	6.2[d]	26.3[d]	−3.86[d]	1.3182[d]
propanoate	30.9[d]	52.3[d]	−4.2[d]	1.2276[d]
decanoate	175.0	181.64	−1.81	0.5372[c]

[a] cal mol^{-1} K^{-1}, [b] cal K mol^{-1}, [c] cal mol^{-1}, [d] Shock and Helgeson (1990), [e] Estimated as discussed in text.

seen that a single correlation fits all the data from Nd^{+3} in the lower left-hand corner to decanoate in the upper right-hand corner. This correlation is given by

$$\sigma = 1.07143\Delta\bar{V}_n^{\circ} + 3.0, \tag{23}$$

which was used extensively in the present study to estimate values of σ for aqueous carboxylic acids and anions.

Values of σ from table 5 or estimated with eq (23) were used to calculate values of the a_2 parameter from the relation

$$\sigma = a_1 + \frac{a_2}{\psi + P}, \tag{24}$$

and values of a_1 estimated from the correlation presented by Shock and Helgeson (1988) and given by

$$a_1 = 1.3684 \times 10^{-2} \left(\frac{\Delta \bar{V}^\circ_n}{41.8393}\right) + 0.1765. \tag{25}$$

In turn, values of a_2 were used to estimate values of a_4 with the correlation expression

$$a_4 = -4.134a_2 - 27790. \tag{26}$$

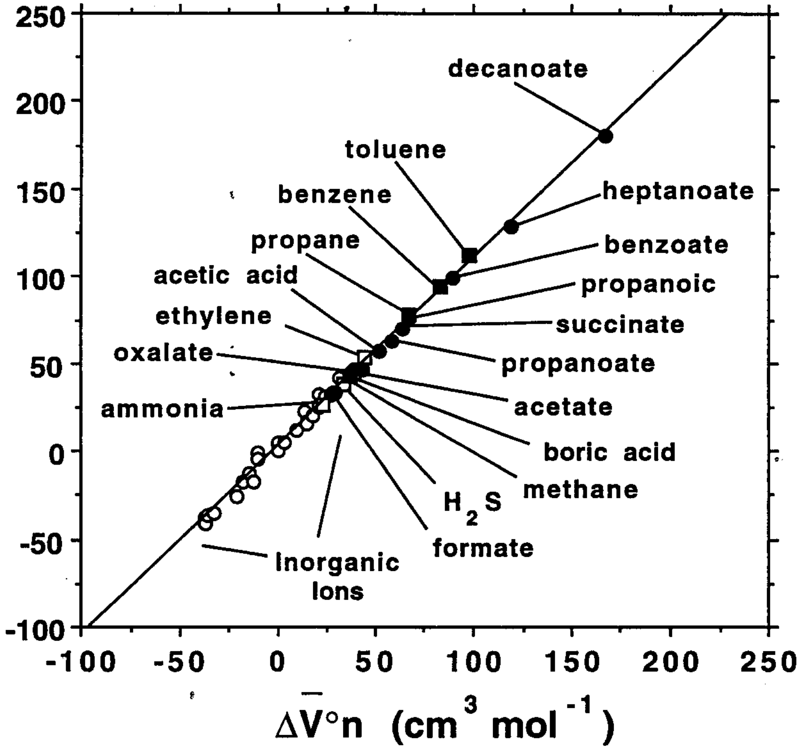


Fig. 8. Correlation of σ with $\Delta\bar{V}^\circ_n$ for aqueous ions (open circles), dissolved gases (open squares), hydrocarbons (solid squares), and carboxylic acid species (solid circles). Curve corresponds to eq (23).

(Shock and Helgeson, 1988), which were then used together with values of a_1, a_2, $\overline{V}^\circ$, and $\Delta\overline{V}^\circ_s$ at 25°C and 1 bar to evaluate a_3 from eq (A-5).

Values of $\overline{C}^\circ_P$ at 25°C and 1 bar and c_2 from table 6 are plotted in figure 9 together with aqueous species from Shock and Helgeson (1990) and Shock (1995), as well as the correlation line for inorganic aqueous species from Shock and Helgeson (1988) and Shock, Helgeson, and Sverjensky (1989). The correlation for inorganic species (lower line) is given by

$$c_2 \times 10^{-4} = 0.2037\overline{C}^\circ_P - 3.9346. \qquad (27)$$

The steeper correlation for neutral aqueous organic species is defined by carboxylic acids and several aqueous hydrocarbons and alcohols evalu-

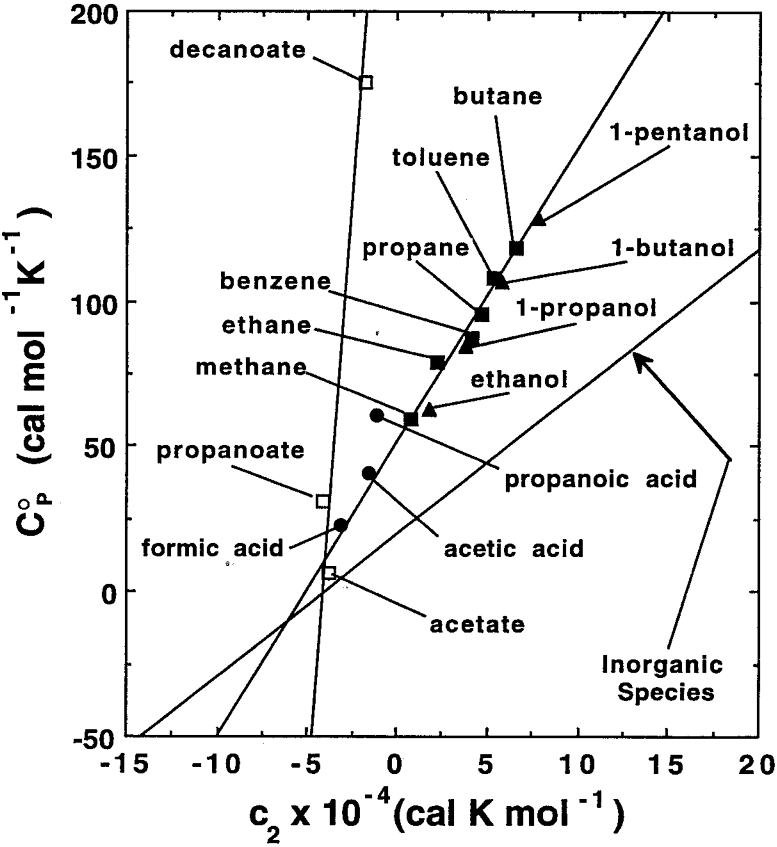


Fig. 9. Correlations of $c_2 \times 10^{-4}$ with $\overline{C}^\circ_P$ for aqueous ions and inorganic neutral species, hydrocarbons and neutral organic acids, and organic anions. Correlation curves are given by eqs (27-29).

ated by Shock (1995) and is consistent with

$$c_2 \times 10^{-4} = 0.0988\overline{C}_P^\circ - 4.961, \quad (28)$$

which was used to estimate values of c_2 for neutral acid species in the absence of experimental data. The steepest correlation in figure 9 is that for the acid anions given by

$$c_2 \times 10^{-4} = 0.01212\overline{C}_P^\circ - 4.106, \quad (29)$$

which yields values of c_2 for carboxylic acid anions which vary only slightly with $\overline{n}$. With the exceptions of oxalate and H-oxalate, eq (29) was used to obtain all other values of c_2 for carboxylate anions estimated in this study. The two oxalic acid anions are unique in that they lack C-H bonds, and it was found that better fits of predicted and experimental log K data were obtained by treating these species as inorganic anions and estimating values of c_2 from eq (27).

COMPARISON OF PREDICTED AND EXPERIMENTAL EQUILIBRIUM DISSOCIATION CONSTANTS AT HIGH PRESSURES AND TEMPERATURES

Standard partial molal properties of aqueous carboxylic acids and acid anions at 25°C and 1 bar adopted in this study are listed in table 4, together with parameters for the revised-HKF equation of state for each species obtained as described in the previous section. The data and parameters in table 4 allow calculation of standard partial molal thermodynamic data for these species, as well as reactions in which they are involved at the elevated temperatures and pressures of geochemical processes. Appropriate equations are summarized in app. 1. Values of $\Delta\overline{G}^\circ$ at elevated temperatures and pressures for carboxylate anions calculated with eq (A-25) and corresponding values for neutral acid species evaluated with eq (A-37) can be used to calculate standard Gibbs free energies of reaction, $\Delta\overline{G}_r^\circ$, from

$$\Delta\overline{G}_r^\circ = \sum_r \nu_{i,r}\Delta\overline{G}^\circ \quad (30)$$

which, in turn, yield values of the equilibrium constant (K) from

$$-2.303RT \log K = \Delta\overline{G}_r^\circ. \quad (31)$$

Comparisons of experimental equilibrium constants with independently calculated values are made in figures 10 to 13 for monocarboxylic, dicarboxylic, and aromatic acids. It can be seen in these figures that in every case there is close agreement between predicted and experimental data. This close agreement supports the validity and generality of the methods used in this study, as well as the usefulness of the predicted log K values listed in table 7 which can be used in the absence of experimental data for a wide variety of geochemical calculations. It should, perhaps, be emphasized that the curves shown in figures 10 to 13 do not represent the results of curve fitting calculations but are constrained by $\overline{V}^\circ$, $\overline{C}_P^\circ$ data, values of log K at 25°C and 1 bar, correlations among thermodynamic data, and between parameters in the revised-HKF equation of state. The theoretical basis of these equations as described in Shock and others (1992) allows accurate extrapolation to regions of pressure and temperature where measurements have not been made, and perhaps cannot be made with current technology, but which are nevertheless encountered in geologic environments.

The comparisons shown in figures 10 to 13 indicate that there is a handful of experimental studies in conflict with the majority of the other experimental data as well as the results of the present study. For example, the highest temperature values of log K for propanoic and n-butanoic acids at P_{SAT} reported by Ellis (1963) and shown in figure 10 are more negative by about 0.2 log K units than the calculated values. In addition, there is disagreement within 0.2 log units between calculated values and some of the high pressure measurements for acetic acid. A few studies of dicarboxylic acid dissociation appear to be inconsistent with the majority of measurements at low temperature as shown in figures 11 and 12. It should be noted that the trend in temperature of the data for the first dissociation of oxalic acid reported by Nikolaeva and Antipina (1972) is inconsistent with the other available data. This is not the case for their second dissociation constants. Divergent temperature trends are also noted in data from Wilson and others (1967) for the toluic acids shown in figure 13. The curves shown in the plot for benzoic acids are *independent* predictions based on the correlations described above, and it can be seen that they are within ±0.2 log K units at all temperatures and pressures.

ESTIMATED DATA FOR HYDROXYACIDS AND PREDICTED EQUILIBRIUM CONSTANTS AT HIGH TEMPERATURES AND PRESSURES

Close agreement between predicted equilibrium constants and their experimental counterparts in figures 10 through 13 is encouraging and suggests that similar success could attend prediction of log K for other organic acids. Experimental data for hydroxyacids are less abundant than the sparse data for carboxylic acids summarized above. Nevertheless hydroxyacids are involved in geochemical processes (Peltzer and Bada, 1981; Cardoso and Eglinton, 1983) and estimation of thermodynamic data could be useful. Experimentally determined standard partial molal data at 25°C and 1 bar for hydroxyacid species are listed in table 8. Although ample $\overline{V}^\circ$ data have been collected, values of $\overline{C}_P^\circ$ and $\Delta\overline{H}_f^\circ$ are considerably more limited, especially for the hydroxy monocarboxylic acids. If additional values of $\Delta\overline{H}_f^\circ$ could be estimated, together with values of $\overline{S}^\circ$ and $\overline{C}_P^\circ$, then the thermodynamic properties of dissociation reactions at 25°C and 1 bar listed in table 9 could be used to evaluate the corresponding data for the anions.[22] Estimates of these properties were made in the present study in the following manner.

---

[22] As in the case of the mono- and dicarboxylic acids (see above), many of the reaction properties adopted in the present study were taken from the comprehensive review of Larson and Hepler (1969). There have been remarkably few experimental studies leading to equilibrium constants or other dissociation reaction properties for hydroxyacids in the 25 yrs since that review. This point is emphasized by the log K data shown in figure 17 which extend from 0° to 50°C for only two of the hydroxyacids. As a group, these organic compounds have been largely ignored by experimentalists and those who analyze oil-field brines and hydrothermal fluids.

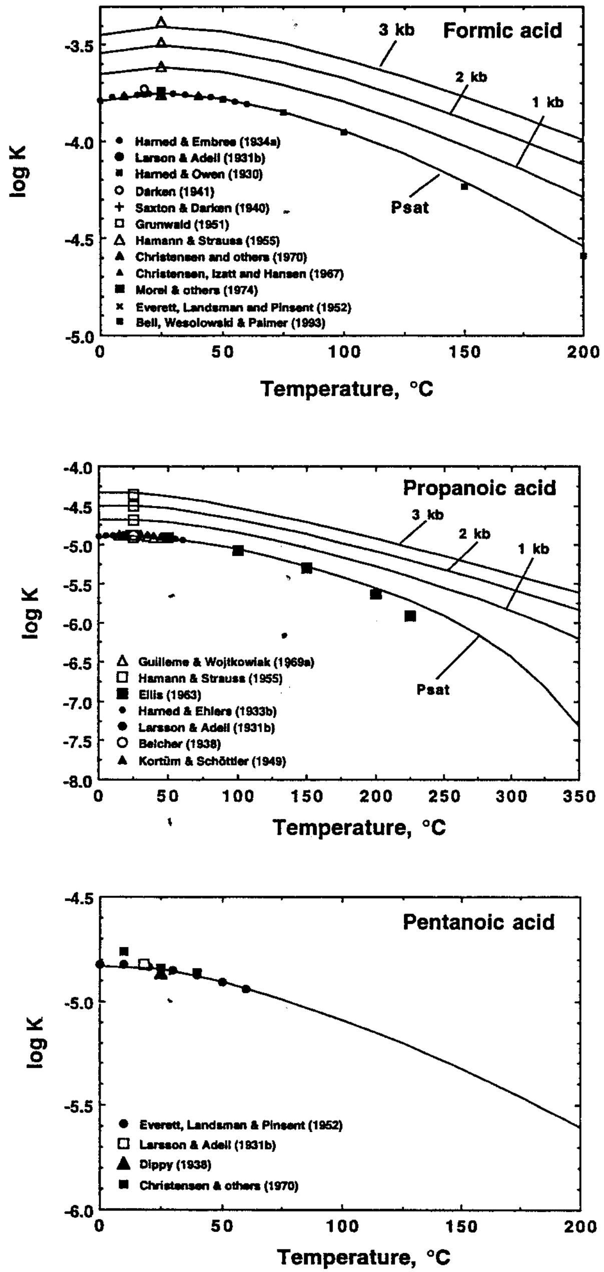


Fig. 10. Log K plotted against temperature for the dissociation of formic, acetic, propanoic, butanoic, pentanoic, and hexanoic acids. Symbols represent experimental data from the references indicated, but curves indicate the results of calculations with the revised-HKF equations of state using data and parameters from table 4. Calculations at P_{SAT} are shown for all acids, and results at 1, 2, and 3 kb for formic, acetic, and propanoic acids are also given.

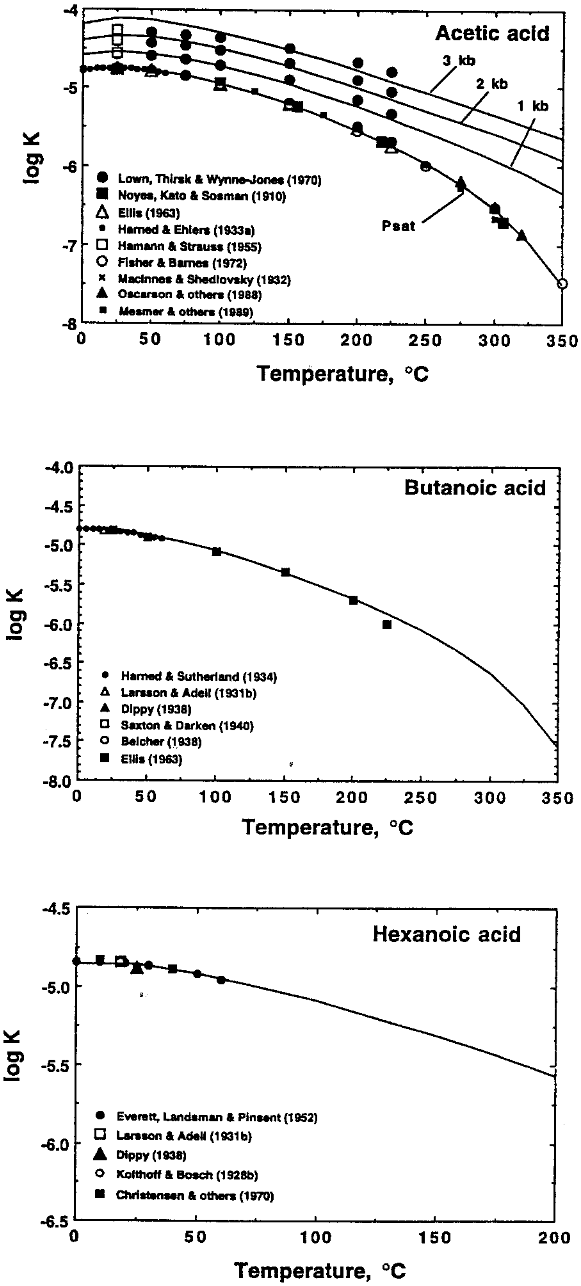


Fig. 10 (continued)

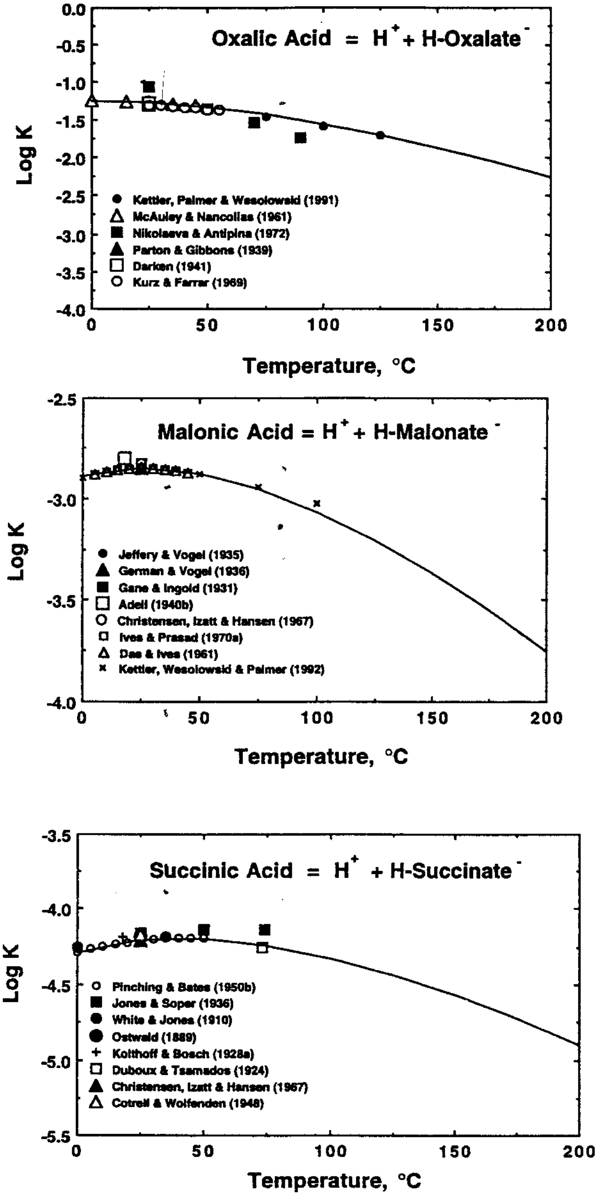


Fig. 11. Log K plotted against temperature at P_{SAT} for the first and second dissociations of oxalic, malonic, and succinic acids. Symbols represent experimental data from the literature sources listed in the figure, but curves were generated in this study with the revised-KHF equations of state together with data and parameters from table 4.

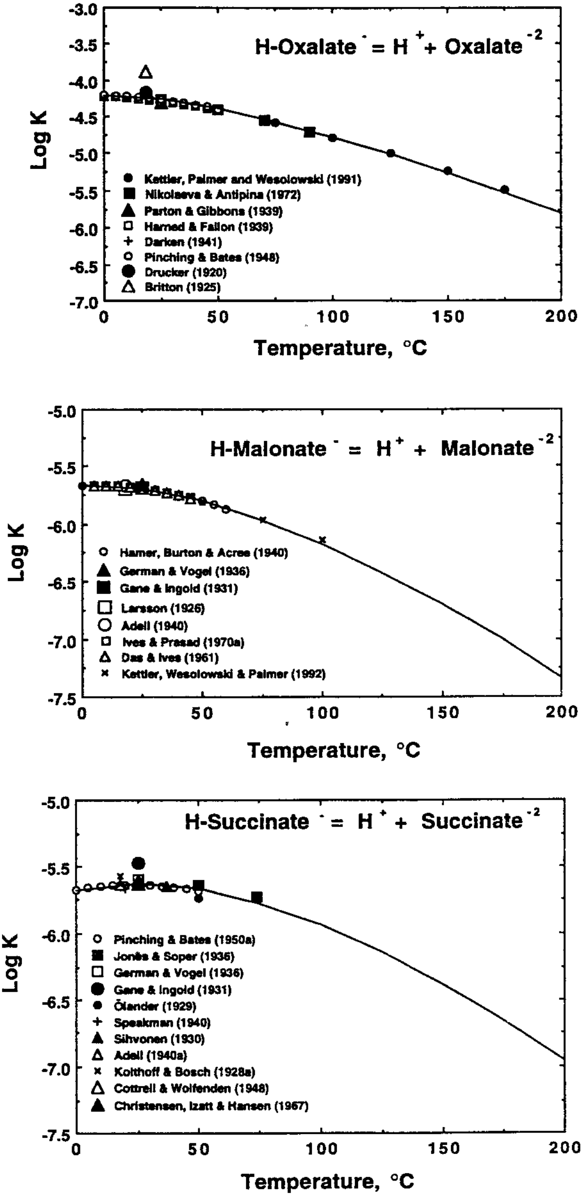


Fig. 11 (continued)

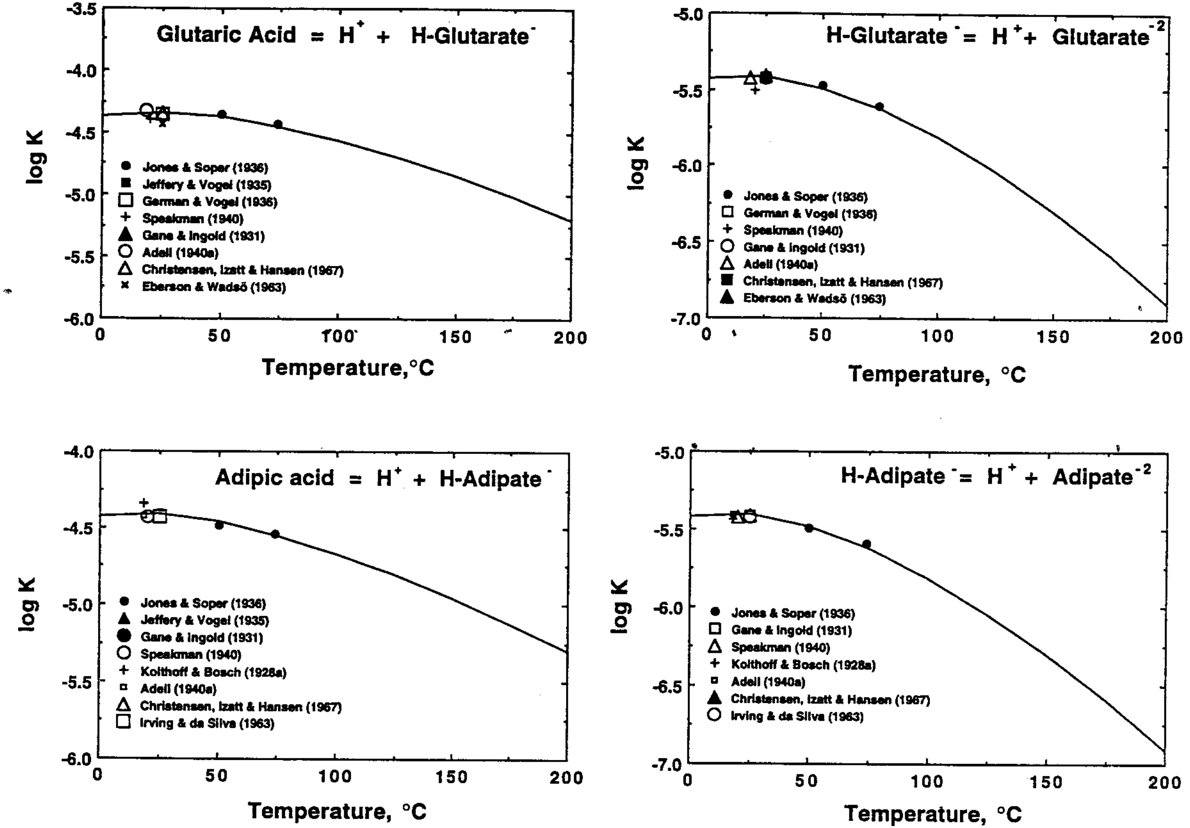


Fig. 12. Log K plotted against temperature at P_{SAT} for the first and second dissociations of glutaric and adipic acids. Symbols represent experimental data from the literature sources listed in the figure, but curves were generated in this study with the revised-HKF equations of state together with data and parameters from table 4.

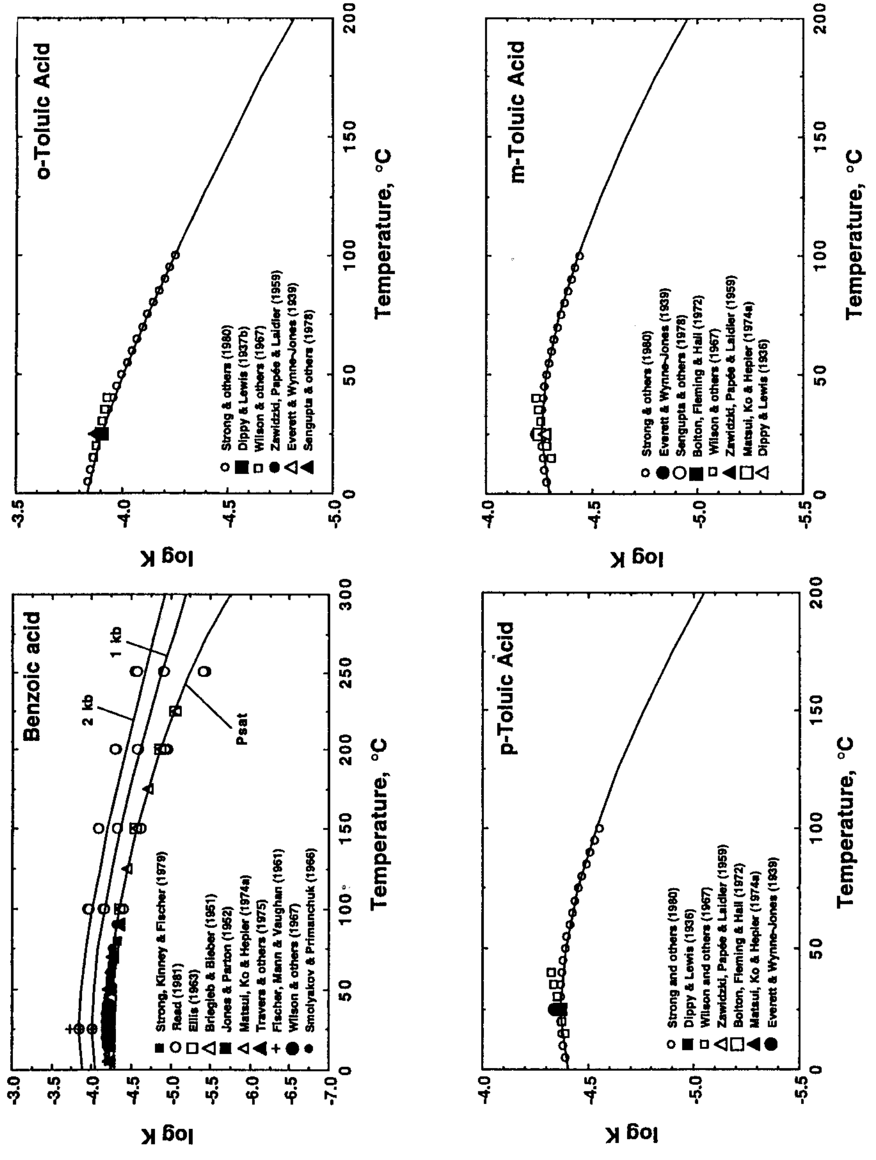


Fig. 13. Plots of log K versus temperature for the dissociation of benzoic, *o*-toluic, *m*-toluic, and *p*-toluic acids. Symbols represent experimental data from the literature sources listed in the figure, but curves correspond to values calculated with the revised-HKF equations of state using data and parameters from table 4. Comparisons are made at P_{SAT} for all four acids and at 1 and 2 kb for benzoic acid.

TABLE 7

Values of log K for carboxylic acid dissociation reactions at various temperatures (in °C) and P_{SAT}, 500 bars, 1000 bars, and 2000 bars, calculated with eqs (32), (33), (A-25), and (A-37) using data and parameters from table 4

P_{SAT}

Acid	0	25	50	75	100	125	150	175	200	225	250	275	300	325	350
Formic	-3.80	-3.75	-3.78	-3.85	-3.95	-4.07	-4.21	-4.37	-4.54	-4.74	-4.97	-5.24	-5.57	-6.01	-6.62
Acetic	-4.78	-4.76	-4.79	-4.85	-4.95	-5.07	-5.21	-5.36	-5.54	-5.74	-5.97	-6.23	-6.55	-6.96	-7.50
Propanoic	-4.91	-4.89	-4.92	-4.98	-5.06	-5.16	-5.28	-5.42	-5.57	-5.75	-5.94	-6.18	-6.46	-6.83	-7.35
Butanoic	-4.80	-4.81	-4.87	-4.96	-5.08	-5.21	-5.35	-5.51	-5.68	-5.87	-6.09	-6.33	-6.63	-7.03	-7.57
Pentanoic	-4.83	-4.85	-4.91	-4.99	-5.09	-5.20	-5.33	-5.46	-5.60	-5.76	-5.94	-6.15	-6.41	-6.75	-7.23
Hexanoic	-4.86	-4.86	-4.92	-5.00	-5.09	-5.20	-5.31	-5.44	-5.57	-5.72	-5.88	-6.07	-6.30	-6.61	-7.04
Heptanoic	-4.89	-4.89	-4.95	-5.02	-5.11	-5.20	-5.31	-5.42	-5.54	-5.66	-5.80	-5.97	-6.16	-6.43	-6.80
Octanoic	-4.90	-4.90	-4.95	-5.03	-5.13	-5.23	-5.34	-5.45	-5.57	-5.70	-5.84	-5.99	-6.18	-6.41	-6.74
Nonanoic	-4.72	-4.73	-4.79	-4.87	-4.96	-5.05	-5.14	-5.23	-5.32	-5.41	-5.52	-5.63	-5.76	-5.94	-6.18
Decanoic	-4.93	-4.92	-4.97	-5.04	-5.11	-5.19	-5.27	-5.35	-5.42	-5.50	-5.58	-5.68	-5.78	-5.91	-6.09
Undecanoic	-4.93	-4.93	-4.97	-5.04	-5.10	-5.16	-5.22	-5.28	-5.33	-5.38	-5.43	-5.49	-5.54	-5.62	-5.70
Dodecanoic	-4.93	-4.92	-4.97	-5.04	-5.12	-5.19	-5.27	-5.33	-5.40	-5.46	-5.51	-5.56	-5.61	-5.66	-5.69
Benzoic	-4.24	-4.20	-4.22	-4.28	-4.36	-4.46	-4.58	-4.72	-4.87	-5.05	-5.24	-5.47	-5.76	-6.13	-6.66
o-Toluic	-3.84	-3.91	-4.01	-4.13	-4.25	-4.38	-4.52	-4.66	-4.81	-4.98	-5.16	-5.37	-5.63	-5.99	-6.48
m-Toluic	-4.30	-4.26	-4.28	-4.35	-4.43	-4.54	-4.66	-4.80	-4.95	-5.12	-5.31	-5.54	-5.81	-6.17	-6.67
p-Toluic	-4.41	-4.37	-4.39	-4.45	-4.54	-4.64	-4.76	-4.90	-5.05	-5.22	-5.41	-5.63	-5.90	-6.26	-6.77
Oxalic (1)	-1.26	-1.27	-1.33	-1.43	-1.56	-1.71	-1.88	-2.07	-2.27	-2.49	-2.74	-3.03	-3.37	-3.81	-4.42
Oxalic (2)	-4.20	-4.26	-4.39	-4.57	-4.78	-5.01	-5.26	-5.53	-5.81	-6.11	-6.44	-6.81	-7.22	-7.72	-8.29
Malonic(1)	-2.89	-2.85	-2.88	-2.96	-3.07	-3.21	-3.37	-3.55	-3.75	-3.98	-4.22	-4.50	-4.83	-5.24	-5.83
Malonic(2)	-5.67	-5.70	-5.80	-5.97	-6.18	-6.42	-6.70	-7.01	-7.34	-7.70	-8.10	-8.54	-9.03	-9.60	-10.34
Succinic(1)	-4.29	-4.21	-4.20	-4.24	-4.33	-4.44	-4.57	-4.73	-4.90	-5.10	-5.32	-5.57	-5.86	-6.23	-6.78
Succinic(2)	-5.68	-5.63	-5.67	-5.78	-5.94	-6.14	-6.38	-6.65	-6.96	-7.29	-7.66	-8.07	-8.54	-9.10	-9.83
Glutaric(1)	-4.37	-4.34	-4.38	-4.46	-4.57	-4.70	-4.85	-5.02	-5.21	-5.41	-5.62	-5.87	-6.15	-6.49	-6.97
Glutaric(2)	-5.43	-5.42	-5.49	-5.63	-5.81	-6.04	-6.30	-6.59	-6.91	-7.25	-7.64	-8.06	-8.55	-9.13	-9.90
Adipic(1)	-4.43	-4.41	-4.46	-4.55	-4.67	-4.81	-4.96	-5.13	-5.31	-5.49	-5.70	-5.92	-6.17	-6.48	-6.90
Adipic(2)	-5.42	-5.41	-5.49	-5.63	-5.82	-6.04	-6.31	-6.60	-6.92	-7.27	-7.65	-8.09	-8.58	-9.17	-9.97
Pimelic(1)	-4.51	-4.49	-4.53	-4.62	-4.73	-4.86	-5.00	-5.15	-5.31	-5.48	-5.66	-5.86	-6.07	-6.33	-6.67
Pimelic(2)	-5.41	-5.42	-5.52	-5.67	-5.87	-6.11	-6.38	-6.68	-7.01	-7.37	-7.76	-8.20	-8.71	-9.32	-10.15
Suberic(1)	-4.53	-4.51	-4.56	-4.64	-4.75	-4.87	-5.00	-5.14	-5.29	-5.44	-5.60	-5.77	-5.96	-6.17	-6.44
Suberic(2)	-5.41	-5.40	-5.48	-5.62	-5.81	-6.04	-6.30	-6.59	-6.91	-7.27	-7.66	-8.09	-8.60	-9.21	-10.07
Azelic(1)	-4.55	-4.52	-4.57	-4.64	-4.74	-4.85	-4.97	-5.09	-5.22	-5.35	-5.48	-5.63	-5.77	-5.94	-6.12
Azelic(2)	-5.40	-5.39	-5.48	-5.62	-5.81	-6.04	-6.30	-6.60	-6.92	-7.27	-7.66	-8.11	-8.62	-9.25	-10.14
Sebacic(1)	-4.57	-4.54	-4.58	-4.66	-4.75	-4.85	-4.96	-5.07	-5.18	-5.29	-5.40	-5.51	-5.63	-5.74	-5.84
Sebacic(2)	-5.43	-5.42	-5.50	-5.64	-5.83	-6.06	-6.32	-6.62	-6.94	-7.29	-7.68	-8.13	-8.65	-9.29	-10.21

500 Bars

Acid	25	50	75	100	125	150	175	200	225	250	275	300	325	350	375	400
Formic	-3.68	-3.71	-3.77	-3.86	-3.97	-4.10	-4.24	-4.39	-4.56	-4.75	-4.95	-5.18	-5.44	-5.74	-6.11	-6.58
Acetic	-4.66	-4.68	-4.74	-4.84	-4.95	-5.08	-5.22	-5.38	-5.56	-5.75	-5.95	-6.19	-6.44	-6.72	-7.07	-7.50
Propanoic	-4.79	-4.80	-4.86	-4.94	-5.03	-5.14	-5.27	-5.40	-5.55	-5.72	-5.90	-6.10	-6.32	-6.58	-6.91	-7.31
Butanoic	-4.69	-4.75	-4.84	-4.95	-5.07	-5.21	-5.35	-5.51	-5.68	-5.86	-6.05	-6.27	-6.51	-6.78	-7.13	-7.56
Pentanoic	-4.73	-4.79	-4.88	-4.98	-5.09	-5.20	-5.33	-5.46	-5.60	-5.74	-5.91	-6.09	-6.29	-6.52	-6.82	-7.20
Hexanoic	-4.74	-4.80	-4.88	-4.98	-5.08	-5.19	-5.31	-5.43	-5.56	-5.70	-5.85	-6.01	-6.19	-6.41	-6.68	-7.02
Heptanoic	-4.77	-4.82	-4.90	-4.99	-5.08	-5.19	-5.29	-5.40	-5.51	-5.63	-5.76	-5.90	-6.06	-6.24	-6.47	-6.77
Octanoic	-4.78	-4.84	-4.93	-5.02	-5.12	-5.23	-5.34	-5.45	-5.57	-5.69	-5.81	-5.95	-6.10	-6.27	-6.48	-6.75
Nonanoic	-4.61	-4.68	-4.76	-4.85	-4.94	-5.03	-5.12	-5.21	-5.29	-5.38	-5.47	-5.57	-5.68	-5.80	-5.95	-6.14
Decanoic	-4.80	-4.86	-4.93	-5.01	-5.09	-5.17	-5.24	-5.32	-5.39	-5.47	-5.54	-5.62	-5.71	-5.80	-5.91	-6.05
Undecanoic	-4.81	-4.86	-4.93	-5.00	-5.06	-5.13	-5.18	-5.24	-5.29	-5.33	-5.38	-5.43	-5.47	-5.52	-5.57	-5.63
Dodecanoic	-4.80	-4.86	-4.93	-5.02	-5.10	-5.17	-5.24	-5.31	-5.37	-5.43	-5.48	-5.53	-5.58	-5.61	-5.65	-5.67
Benzoic	-4.10	-4.12	-4.18	-4.26	-4.36	-4.47	-4.60	-4.73	-4.88	-5.05	-5.22	-5.43	-5.65	-5.91	-6.24	-6.66
o-Toluic	-3.81	-3.91	-4.03	-4.15	-4.28	-4.41	-4.54	-4.67	-4.82	-4.97	-5.12	-5.31	-5.51	-5.74	-6.04	-6.42
m-Toluic	-4.16	-4.19	-4.25	-4.34	-4.44	-4.56	-4.68	-4.82	-4.97	-5.13	-5.30	-5.49	-5.71	-5.96	-6.28	-6.67
p-Toluic	-4.27	-4.30	-4.36	-4.44	-4.54	-4.65	-4.78	-4.91	-5.06	-5.22	-5.39	-5.58	-5.80	-6.05	-6.37	-6.77
Oxalic (1)	-1.21	-1.27	-1.37	-1.49	-1.64	-1.79	-1.97	-2.15	-2.35	-2.56	-2.79	-3.04	-3.32	-3.63	-4.02	-4.51
Oxalic (2)	-4.16	-4.29	-4.47	-4.67	-4.89	-5.13	-5.38	-5.63	-5.91	-6.19	-6.49	-6.81	-7.14	-7.48	-7.88	-8.29
Malonic(1)	-2.77	-2.80	-2.88	-2.98	-3.12	-3.28	-3.45	-3.64	-3.84	-4.06	-4.30	-4.55	-4.84	-5.17	-5.52	-6.01
Malonic(2)	-5.54	-5.65	-5.81	-6.02	-6.26	-6.53	-6.82	-7.14	-7.47	-7.83	-8.20	-8.60	-9.03	-9.53	-9.90	-10.43
Succinic(1)	-4.10	-4.10	-4.14	-4.23	-4.33	-4.46	-4.61	-4.78	-4.96	-5.15	-5.36	-5.59	-5.85	-6.16	-6.48	-6.92
Succinic(2)	-5.51	-5.55	-5.66	-5.81	-6.01	-6.24	-6.50	-6.78	-7.08	-7.41	-7.76	-8.14	-8.55	-9.02	-9.39	-9.92
Glutaric(1)	-4.23	-4.27	-4.35	-4.46	-4.60	-4.75	-4.91	-5.09	-5.27	-5.47	-5.68	-5.91	-6.16	-6.44	-6.74	-7.14
Glutaric(2)	-5.30	-5.37	-5.51	-5.69	-5.91	-6.16	-6.43	-6.73	-7.05	-7.39	-7.75	-8.14	-8.57	-9.06	-9.46	-10.02
Adipic(1)	-4.30	-4.36	-4.45	-4.57	-4.71	-4.86	-5.02	-5.19	-5.37	-5.56	-5.76	-5.97	-6.20	-6.46	-6.72	-7.07
Adipic(2)	-5.29	-5.37	-5.51	-5.70	-5.92	-6.17	-6.44	-6.74	-7.06	-7.41	-7.77	-8.17	-8.60	-9.09	-9.51	-10.11
Pimelic(1)	-4.37	-4.42	-4.51	-4.62	-4.75	-4.89	-5.04	-5.20	-5.37	-5.54	-5.72	-5.90	-6.10	-6.32	-6.54	-6.83
Pimelic(2)	-5.31	-5.40	-5.55	-5.75	-5.98	-6.24	-6.53	-6.83	-7.16	-7.51	-7.88	-8.29	-8.73	-9.24	-9.69	-10.33
Suberic(1)	-4.40	-4.45	-4.54	-4.65	-4.78	-4.91	-5.05	-5.19	-5.34	-5.50	-5.65	-5.82	-5.99	-6.17	-6.35	-6.58
Suberic(2)	-5.29	-5.37	-5.51	-5.69	-5.91	-6.16	-6.44	-6.74	-7.06	-7.41	-7.77	-8.17	-8.61	-9.12	-9.59	-10.26
Azelic(1)	-4.41	-4.46	-4.55	-4.65	-4.76	-4.88	-5.00	-5.13	-5.26	-5.40	-5.53	-5.67	-5.81	-5.96	-6.09	-6.24
Azelic(2)	-5.28	-5.36	-5.50	-5.69	-5.91	-6.17	-6.44	-6.74	-7.07	-7.41	-7.78	-8.19	-8.63	-9.15	-9.65	-10.35
Sebacic(1)	-4.44	-4.48	-4.56	-4.66	-4.76	-4.87	-4.99	-5.10	-5.21	-5.33	-5.44	-5.55	-5.66	-5.78	-5.85	-5.94
Sebacic(2)	-5.31	-5.39	-5.53	-5.71	-5.93	-6.18	-6.46	-6.76	-7.08	-7.43	-7.80	-8.21	-8.66	-9.18	-9.71	-10.45

TABLE 7 *(continued)*

1000 Bars

Acid	50	100	150	200	250	300	350	400	450	500	550	600
Formic	-3.64	-3.78	-4.01	-4.27	-4.58	-4.93	-5.33	-5.82	-6.43	-7.17	-8.12	-9.21
Acetic	-4.57	-4.72	-4.96	-5.24	-5.57	-5.93	-6.35	-6.83	-7.42	-8.11	-8.96	-9.93
Propanoic	-4.71	-4.83	-5.02	-5.26	-5.54	-5.85	-6.21	-6.64	-7.18	-7.82	-8.63	-9.55
Butanoic	-4.64	-4.83	-5.08	-5.37	-5.68	-6.02	-6.41	-6.86	-7.43	-8.11	-8.97	-9.95
Pentanoic	-4.68	-4.87	-5.09	-5.33	-5.59	-5.87	-6.18	-6.56	-7.05	-7.63	-8.39	-9.27
Hexanoic	-4.69	-4.87	-5.09	-5.31	-5.55	-5.81	-6.10	-6.45	-6.88	-7.42	-8.10	-8.89
Heptanoic	-4.71	-4.88	-5.08	-5.28	-5.49	-5.71	-5.96	-6.26	-6.63	-7.09	-7.68	-8.36
Octanoic	-4.74	-4.93	-5.13	-5.35	-5.57	-5.79	-6.04	-6.32	-6.66	-7.08	-7.60	-8.19
Nonanoic	-4.58	-4.76	-4.94	-5.11	-5.27	-5.43	-5.60	-5.80	-6.04	-6.33	-6.70	-7.13
Decanoic	-4.75	-4.91	-5.08	-5.23	-5.37	-5.50	-5.64	-5.79	-5.97	-6.18	-6.44	-6.74
Undecanoic	-4.76	-4.90	-5.04	-5.15	-5.24	-5.32	-5.40	-5.47	-5.56	-5.65	-5.76	-5.88
Dodecanoic	-4.75	-4.92	-5.08	-5.22	-5.35	-5.45	-5.54	-5.61	-5.67	-5.70	-5.72	-5.74
Benzoic	-4.04	-4.17	-4.37	-4.62	-4.89	-5.21	-5.56	-6.00	-6.54	-7.20	-8.04	-9.01
o-Toluic	-3.83	-4.07	-4.31	-4.56	-4.81	-5.09	-5.39	-5.77	-6.24	-6.83	-7.60	-8.48
m-Toluic	-4.10	-4.25	-4.46	-4.71	-4.98	-5.28	-5.63	-6.04	-6.56	-7.19	-7.99	-8.91
p-Toluic	-4.21	-4.35	-4.56	-4.80	-5.07	-5.37	-5.71	-6.13	-6.65	-7.28	-8.09	-9.02
Oxalic (1)	-1.22	-1.44	-1.72	-2.06	-2.42	-2.83	-3.28	-3.82	-4.47	-5.24	-6.22	-7.32
Oxalic (2)	-4.20	-4.58	-5.02	-5.49	-6.00	-6.53	-7.09	-7.70	-8.37	-9.07	-9.85	-10.69
Malonic(1)	-2.72	-2.91	-3.20	-3.54	-3.94	-4.37	-4.85	-5.40	-6.06	-6.88	-7.88	-8.98
Malonic(2)	-5.50	-5.88	-6.38	-6.97	-7.61	-8.30	-9.04	-9.83	-10.69	-11.66	-12.75	-13.88
Succinic(1)	-4.00	-4.13	-4.37	-4.67	-5.02	-5.41	-5.85	-6.35	-6.95	-7.71	-8.64	-9.65
Succinic(2)	-5.45	-5.70	-6.12	-6.63	-7.22	-7.86	-8.56	-9.32	-10.16	-11.13	-12.22	-13.38
Glutaric(1)	-4.17	-4.37	-4.65	-4.99	-5.35	-5.75	-6.17	-6.65	-7.21	-7.90	-8.72	-9.62
Glutaric(2)	-5.27	-5.59	-6.04	-6.59	-7.20	-7.87	-8.59	-9.38	-10.26	-11.27	-12.45	-13.69
Adipic(1)	-4.26	-4.48	-4.77	-5.10	-5.45	-5.83	-6.23	-6.66	-7.17	-7.76	-8.48	-9.25
Adipic(2)	-5.27	-5.59	-6.05	-6.60	-7.22	-7.89	-8.62	-9.42	-10.32	-11.38	-12.62	-13.95
Pimelic(1)	-4.31	-4.52	-4.80	-5.11	-5.43	-5.77	-6.13	-6.51	-6.94	-7.43	-8.01	-8.62
Pimelic(2)	-5.30	-5.64	-6.12	-6.69	-7.32	-8.00	-8.75	-9.57	-10.51	-11.63	-12.95	-14.38
Suberic(1)	-4.36	-4.57	-4.83	-5.11	-5.40	-5.71	-6.02	-6.34	-6.70	-7.10	-7.55	-8.02
Suberic(2)	-5.26	-5.59	-6.05	-6.60	-7.21	-7.89	-8.63	-9.46	-10.42	-11.57	-12.95	-14.44
Azelic(1)	-4.37	-4.56	-4.80	-5.05	-5.31	-5.58	-5.84	-6.10	-6.38	-6.66	-6.97	-7.28
Azelic(2)	-5.26	-5.59	-6.05	-6.60	-7.22	-7.90	-8.65	-9.50	-10.48	-11.69	-13.14	-14.72
Sebacic(1)	-4.39	-4.57	-4.79	-5.03	-5.26	-5.48	-5.70	-5.90	-6.09	-6.26	-6.41	-6.56
Sebacic(2)	-5.28	-5.61	-6.07	-6.62	-7.23	-7.92	-8.67	-9.53	-10.55	-11.80	-13.34	-15.01

2000 Bars

Acid	50	100	150	200	250	300	350	400	450	500	550	600	650	700	750
Formic	-3.53	-3.66	-3.86	-4.09	-4.35	-4.63	-4.94	-5.27	-5.65	-6.05	-6.45	-6.89	-7.35	-7.85	-8.36
Acetic	-4.36	-4.51	-4.73	-5.00	-5.29	-5.60	-5.93	-6.29	-6.69	-7.10	-7.52	-7.96	-8.42	-8.91	-9.41
Propanoic	-4.54	-4.64	-4.82	-5.04	-5.28	-5.54	-5.82	-6.13	-6.47	-6.83	-7.20	-7.58	-8.00	-8.44	-8.89
Butanoic	-4.45	-4.63	-4.87	-5.14	-5.42	-5.70	-6.01	-6.34	-6.70	-7.08	-7.45	-7.86	-8.29	-8.75	-9.21
Pentanoic	-4.49	-4.69	-4.91	-5.13	-5.36	-5.59	-5.83	-6.10	-6.39	-6.70	-7.01	-7.34	-7.70	-8.08	-8.47
Hexanoic	-4.50	-4.69	-4.90	-5.12	-5.33	-5.55	-5.78	-6.02	-6.29	-6.57	-6.85	-7.15	-7.48	-7.82	-8.17
Heptanoic	-4.52	-4.69	-4.89	-5.08	-5.27	-5.46	-5.66	-5.86	-6.09	-6.33	-6.57	-6.82	-7.10	-7.39	-7.68
Octanoic	-4.56	-4.75	-4.97	-5.18	-5.38	-5.58	-5.78	-5.99	-6.21	-6.44	-6.67	-6.91	-7.17	-7.43	-7.71
Nonanoic	-4.39	-4.58	-4.77	-4.94	-5.09	-5.23	-5.37	-5.51	-5.66	-5.81	-5.96	-6.12	-6.29	-6.47	-6.65
Decanoic	-4.57	-4.74	-4.91	-5.07	-5.20	-5.32	-5.44	-5.56	-5.68	-5.80	-5.91	-6.03	-6.16	-6.29	-6.42
Undecanoic	-4.57	-4.73	-4.88	-5.00	-5.09	-5.17	-5.23	-5.29	-5.35	-5.40	-5.45	-5.50	-5.55	-5.60	-5.65
Dodecanoic	-4.55	-4.74	-4.92	-5.07	-5.20	-5.31	-5.40	-5.48	-5.55	-5.61	-5.66	-5.70	-5.74	-5.78	-5.82
Benzoic	-3.88	-4.01	-4.21	-4.43	-4.68	-4.94	-5.21	-5.52	-5.86	-6.21	-6.58	-6.96	-7.38	-7.82	-8.27
o-Toluic	-3.67	-3.91	-4.15	-4.38	-4.60	-4.82	-5.05	-5.29	-5.57	-5.86	-6.15	-6.47	-6.81	-7.18	-7.56
m-Toluic	-3.94	-4.10	-4.30	-4.53	-4.77	-5.03	-5.30	-5.59	-5.91	-6.25	-6.60	-6.97	-7.36	-7.77	-8.20
p-Toluic	-4.05	-4.20	-4.40	-4.62	-4.86	-5.11	-5.37	-5.66	-5.99	-6.33	-6.67	-7.04	-7.44	-7.86	-8.28
Oxalic (1)	-1.13	-1.34	-1.61	-1.91	-2.24	-2.59	-2.95	-3.34	-3.77	-4.22	-4.67	-5.14	-5.65	-6.18	-6.71
Oxalic (2)	-4.04	-4.41	-4.84	-5.28	-5.73	-6.19	-6.66	-7.15	-7.67	-8.19	-8.70	-9.22	-9.76	-10.33	-10.92
Malonic(1)	-2.59	-2.78	-3.06	-3.39	-3.75	-4.14	-4.55	-4.97	-5.42	-5.89	-6.38	-6.90	-7.43	-7.95	-8.47
Malonic(2)	-5.25	-5.63	-6.13	-6.69	-7.29	-7.91	-8.56	-9.22	-9.90	-10.59	-11.30	-12.03	-12.76	-13.48	-14.19
Succinic(1)	-3.83	-3.97	-4.21	-4.50	-4.82	-5.17	-5.54	-5.92	-6.33	-6.76	-7.22	-7.70	-8.18	-8.67	-9.15
Succinic(2)	-5.26	-5.51	-5.91	-6.39	-6.93	-7.51	-8.11	-8.74	-9.38	-10.05	-10.74	-11.45	-12.17	-12.88	-13.57
Glutaric(1)	-3.99	-4.20	-4.49	-4.81	-5.16	-5.52	-5.90	-6.28	-6.68	-7.09	-7.52	-7.97	-8.42	-8.87	-9.31
Glutaric(2)	-5.08	-5.40	-5.84	-6.36	-6.92	-7.52	-8.14	-8.79	-9.45	-10.14	-10.85	-11.58	-12.32	-13.05	-13.76
Adipic(1)	-4.08	-4.31	-4.61	-4.93	-5.27	-5.62	-5.98	-6.34	-6.71	-7.09	-7.48	-7.89	-8.29	-8.70	-9.09
Adipic(2)	-5.08	-5.40	-5.85	-6.37	-6.94	-7.54	-8.16	-8.81	-9.48	-10.18	-10.90	-11.64	-12.40	-13.15	-13.88
Pimelic(1)	-4.12	-4.35	-4.63	-4.94	-5.26	-5.58	-5.91	-6.24	-6.57	-6.90	-7.25	-7.60	-7.95	-8.29	-8.63
Pimelic(2)	-5.11	-5.46	-5.92	-6.46	-7.04	-7.65	-8.29	-8.95	-9.63	-10.34	-11.08	-11.84	-12.62	-13.39	-14.14
Suberic(1)	-4.18	-4.41	-4.68	-4.96	-5.25	-5.55	-5.83	-6.12	-6.41	-6.70	-6.99	-7.28	-7.57	-7.86	-8.14
Suberic(2)	-5.08	-5.40	-5.85	-6.37	-6.94	-7.54	-8.17	-8.82	-9.50	-10.21	-10.96	-11.73	-12.51	-13.29	-14.05
Azelic(1)	-4.19	-4.40	-4.65	-4.91	-5.18	-5.43	-5.69	-5.94	-6.18	-6.42	-6.65	-6.89	-7.12	-7.34	-7.56
Azelic(2)	-5.08	-5.41	-5.86	-6.38	-6.95	-7.55	-8.18	-8.84	-9.53	-10.25	-11.00	-11.79	-12.59	-13.39	-14.17
Sebacic(1)	-4.21	-4.42	-4.65	-4.89	-5.13	-5.36	-5.58	-5.79	-5.99	-6.18	-6.36	-6.53	-6.70	-6.86	-7.01
Sebacic(2)	-5.10	-5.42	-5.87	-6.39	-6.95	-7.56	-8.19	-8.85	-9.54	-10.27	-11.04	-11.84	-12.66	-13.48	-14.28

TABLE 8

Standard partial molal properties of aqueous hydroxyacids and anions at 25°C and 1 bar from experimental measurements

Species	$\Delta\overline{H}_f^{\circ}$[a]	$\overline{V}^{\circ}$[b]	$\overline{C}_P^{\circ}$[s]
glycolic acid	-154890.[c]	51.75[d]	
lactic acid	-164000.[e]	69.38[d]	
	-164020.[m]		
2-hydroxybutanoic acid		85.45[d]	
2-hydroxypentanoic acid		100.47[d]	
2-hydroxyhexanoic acid		117.26[d]	
2-hydroxyisobutanoic acid		86.78[d]	
2-hydroxyisopentanoic acid		100.83[d]	
DL-malic acid	-259040.[e]	82.80[g]	56.4[g]
	-259050.[q]	82.22[f]	
L-tartaric acid	-302750.[q]	83.99[d]	60.0[g]
		83.45[n]	
		82.23[f]	
		83.4[g]	77.1[g]
citric acid	-364650.[q]	113.60[g]	
		112.44[f]	
		114.7[h]	
ascorbic acid	-272770.[r]	105.17[i]	
glycolate		39.85[j]	
lactate		56.25[j]	
2-hydroxybutanoate		71.61[j]	
2-hydroxypentanoate		86.71[j]	
2-hydroxyhexanaoate		103.33[j]	
2-hydroxyisobutanoate		72.63[j]	
2-hydroxyisopentanoate		86.84[j]	
H-tartrate		71.94[j]	
tartrate		58.48[j]	
		58.78[p]	
o-hydroxybenzoate		94.81[k]	46.99[l]
m-hydroxybenzoate		90.01[k]	38.84[l]
p-hydroxybenzoate		88.65[k]	38.07[l]

[a] cal mol^{-1}, [b] cm^3 mol^{-1}, [c] Miller and Smith-Magowan (1990), corrected in present study [d] Høiland and Vikingstad (1975), [e] Miller and Smith-Magowan (1990), [f] Manzurola and Apelblat (1985), [g] Sijpkes and others (1989), [h] Levien (1955), [i] Apelblat and Manzurola (1989), [j] Calculated from $\overline{V}^{\circ}$ of the aqueous sodium electrolyte from Høiland andVikingstand (1975), together with V° for Na$^+$ from Shock and Helgeson (1988), [k] Calculated from $\overline{V}^{\circ}$ of the acqueous sodium electrolyte from Desnoyers and others (1973), together with $\overline{V}^{\circ}$ for Na$^+$ from Shock and Helgeson (1988), [l] Calculated from $\overline{C}_P^{\circ}$ of the aqueous sodium electrolyte from Desnoyers and others (1973) together with $\overline{C}_P^{\circ}$ for Na$^+$ from Shock and Helgeson (1988), [m] Saville and Gundry (1959), [n] Mathieson and Conway (1975), [p] Calculated from the value for the aqueous potassium electrolyte given by Mathieson and Conway (1975) and the value of $\overline{V}^{\circ}$ for K$^+$ from Shock and Helgeson (1988), [q] Calculated from ΔH° (s → aq) given by Apelblat (1986) and ΔH_f° of the solid from Domalski (1972), [r] Calculated from ΔH° (s → aq) given by Apelblat (1990) and ΔH_f° of the solid from Domalski (1972), [s] cal mol^{-1} K^{-1}.

TABLE 9

Standard molal thermodynamic properties of dissociation for aqueous hydroxyacids at 25°C and 1 bar from the literature[a]

Acid	ΔG°_{D}[b]		ΔH°_{D}[b]		ΔS°_{D}[c]		$\Delta C^{\circ}_{P,D}$[c]		$\Delta V^{\circ}_{P,D}$[d]
glycolic	5230.[e,g]	5227.[i]	170.[e]	160.[g]	-16.9[e]	-17.0[g]	-39.[e]	-31.[ae]	-11.9[y]
	5226.[ap]	5215.[h]	150.[ae]	110.[as]	-17.1[ae]	-17.2[as]			
	5245.[ae]	5210.[aq]							
	5270.[j]								
lactic	5270.[e,h,am]	5266.[g]	-70.[e]	-80.[g]	-17.9[e,g]		-40.[e]	-13.13[y]	
2-hydroxybutanoic	5200.[n]		-13.84[y]						
3-hydroxybutanoic	6000.[n]								
n-hydroxypentanoic	4900.[p]								
o-hydroxybenzoic	4060.[e]	4050.[k,l,u,at]	730.[e,u]	800.[v]	-11.2[e,u]	-10.9[v]	-7.8[ab]		
(salicylic)	4070.[v,w]	4054.[ak]	1500.[ad]		-8.7[ad]				
	4021.[af]	4090.[ac]							
	4100.[ad]	4080.[an]							
	3760.[ar]								
m-hydroxybenzoic	5560.[e,m,t]	5540.[an]	160.[e,t]		-18.1[e,m]		-34.[e]		
	5325.[ar]	5570.[x]	159.[m]		-18.12[t]		-38.[m]		
p-hydroxybenzoic	6250.[e,q,s,t,x]	6270.[m]	400.[e]	363.[m]	-19.6[e]	-9.8[m]	-42.[e]		
	6290.[aa]	6200.[ad]	540.[q]	1600.[ad]	-19.1[q,r]	-15.4[ad]			
	6190.[m]	5850.[ar]	30.5[r]	386.[s]	-19.66[s]	-19.72[t]			
	5730.[r]		370.[t]						
malic (1)	4720.[e,f,k]	4726.[af]	710.[e]		-13.4[e]		-37.[e]		
(2)	6950.[e]	6967.[af]	280.[e]		-24.1[e]		-54.[e]		
	6890.[f,k]								
L-tartaric (1)	4140.[e,z]	4135.[af]	740.[e]		-11.4[e]		-42.[e]	-12.05[y]	
	3440.[f]								
(2)	5960.[e,z,af]	5680.[f]	200.[e]		-19.3[e]		-53.[e]	-13.46[y]	
D-tartaric (1)	4110.[ak]								
(2)	6185.[ak]								
citric (1)	4268.[ag,af]	4266.[ah]	997.[ag]	940.[ai]	-11.0[ag,ai]		-31.8[ag]		
	4170.[ai]	4203.[aj]							
(2)	6491.[ag]	6522.[ah]	583.[ag]	408.[ai]	-19.8[ag]	-20.[ai]	-44.7[ag]		
	6492.[ai]	6360.[aj]							
	6518.[af]	6468.[al]							
(3)	8726.[ag]	8768.[ah]	-803.[ag]	-754.[ai]	-32.0[ag,ai]		-61.2[ag]		
	8731.[ai]	8705.[aj]							
	8749.[af]	8542.[al]							

[a] The subscript D refers to the dissociation reaction, [b] cal mol^{-1}, [c] cal mol^{-1} K^{-1}, [d] cm^{3} mol^{-1}, [e] Larson and Hepler (1969), [f] Topp and Davies (1940), [g] Smith and Martell (1989), [h] Davies and Monk (1954), [i] Nims (1936), [j] Lloyd, Wycherley, and Monk (1951), [k] Bell and Waind (1951), [l] Davies (1938), [m] Cottrell and others (1948), [n] Crutchfield, McNabb, and Hazel (1962), [p] Gouveia and DeCarvahlo (1968), [q] Bell (1959), [r] Pal'chevskii, Zakharyevskii, and Malinina (1960), [s] Wilson and others (1967), [t] Matsui, Ko, and Hepler (1974a), [u] Ernst, Irving and Menashi (1964), [v] Vasil'ev and Kochergina (1967), [w] Minnick and Kilpatrick (1939), [x] Briegleb and Bieber (1951), [y] Calculated from data in table 8, [z] Bates and Canham (1951), [aa] Mattoo (1956), [ab] Lown, Thirsk, and Wynne-Jones (1968), [ac] Lowe and Smith (1975b), [ad] Hermans, Leach, and Scheraga (1963), [ae] Christensen, Oscarson, and Izatt (1968), [af] De Robertis and others (1990), [ag] Bates and Pinching (1949), [ah] Litchinsky and others (1969), [ai] Bjerrum and Unmack (1929), [aj] Heinz (1951), [ak] Sartori, Costa and Camus (1952), [al] Simms (1928a,b), [am] Nims and Smith (1936), [an] Larsson (1929), [ap] Bell and Kuhn (1963), [aq] Adell (1940b), [ar] Abichandani and Jatkar (1938), [as] Christensen, Izatt, and Hansen (1967), [at] Dudeney and Irving (1975).

Correlations at 25°C and 1 bar.—Values of $\overline{V}^\circ$ from table 8 for straight-chain hydroxyacids and anions are plotted against $\overline{n}$ in figure 14 where it can be seen that $\overline{V}^\circ$ data for these aqueous organic species are consistent with

$$\overline{V}^\circ = 15.8\,\overline{n} + 21.5 \tag{32}$$

for the acids, and

$$\overline{V}^\circ = 15.8\,\overline{n} + 8.0 \tag{33}$$

for the anions, respectively. It should be noted that the slopes of these correlation curves are identical to those of all other $\overline{V}^\circ$ versus $\overline{n}$ correlations for homologous series of aqueous compounds (see fig. 1 above and Shock and Helgeson, 1990). Comparison of eqs (32) and (33) with eqs (1) and (2) shows that the effect on $\overline{V}^\circ$ of the transformation from monocarboxylic species to hydroxyacid species is small and on the order of ~ 1.0 cm^3 mol^{-1}.

As emphasized above, correlations of $\Delta\overline{H}_f^\circ$ versus $\overline{n}$ for homologous series of compounds also share a common slope. By assuming that the properties of the higher homologues would be more like lactic acid than the first member of the series, glycolic acid (see above), the following expression was generated using the value of $\Delta\overline{H}_f^\circ$ for lactic acid in table 8

$$\Delta\overline{H}_f^\circ = -5670\,\overline{n} - 146990. \tag{34}$$

This expression serves as a first approximation of the $\Delta\overline{H}_f^\circ$ versus $\overline{n}$ correlation for hydroxyacids which should be tested by further experimental measurements. Note that the value of $\Delta\overline{H}_f^\circ$ for glycolic acid in table 8 is more positive than the corresponding value calculated from eq (34), which is completely consistent with the behavior of the first member of many other homologous series of neutral aqueous organic compounds (Shock and Helgeson, 1990; Schulte and Shock, 1993), as well as the carboxylic acids shown in figures 3 and 5. Values of $\Delta\overline{G}_f^\circ$ for hydroxyacids can be calculated from these estimates of $\Delta\overline{H}_f^\circ$ if values of $\overline{S}^\circ$ are estimated.

In the present study, values of $\overline{S}^\circ$ for hydroxyacids were estimated by comparison to other aqueous organic compounds that contain the hydroxyl group. For example, the correlations of $\overline{S}^\circ$ versus $\overline{n}$ found by Shock and Helgeson (1990) for the alkanes and primary alcohols are given by

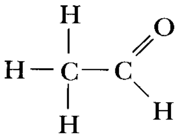
$$\overline{S}^\circ = 6.7\,\overline{n} + 12.8, \tag{35}$$

and

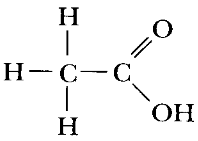
$$\overline{S}^\circ = 6.7\,\overline{n} + 23.2, \tag{36}$$

respectively. The difference in intercepts between these two curves is 10.4 cal mol^{-1} K^{-1}. This value compares well with the difference in $\bar{S}^\circ$ between phenol and benzene (10.3 cal mol^{-1} K^{-1}) calculated from data tabulated by Shock and Helgeson (1990). This suggests that about 10.4 cal mol^{-1} K^{-1} in $\bar{S}^\circ$ attends the removal of a proton and replacement with a hydroxyl group in the transformation of a hydrocarbon into an alcohol. This transformation also characterizes the difference between carboxylic acids and hydroxyacids. However, in the case of the alkane to alcohol transformation, a hydrophobic, slightly-soluble compound is converted into one which is hydrophilic and highly-soluble. Both carboxylic and hydroxyacids are highly hydrophilic compounds, and it would seem that the transformation between them is less dramatic than that between alkanes and alcohols. As a consequence, it is likely that differences in thermodynamic properties between two analogous hydrophilic compounds should be less than that between an alkane and an alcohol. Evidence that this is the case is observed in the $\bar{V}^\circ$ data discussed above and can be extracted from a comparison of the properties of acetaldehyde and acetic acid.

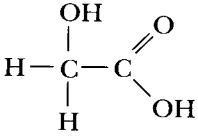
In the transformation of acetaldehyde



into acetic acid,



a hydrogen must be removed and replaced with a hydroxyl group. A similar transformation attends the conversion of acetic acid into glycolic acid



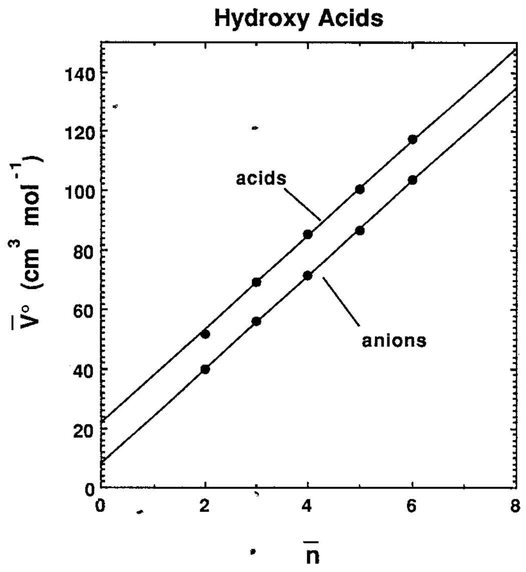


Fig. 14. Standard partial molal volumes of aqueous hydroxyacids and anions at 25°C and 1 bar from table 8, plotted against the number of moles of carbon in their stoichiometric formulas ($\bar{n}$). The correlation curves are given by eqs. (32) and (33).

As discussed by Schulte and Shock (1993), thermodynamic data for aqueous aldehydes are scarce. Data for formaldehyde and acetaldehyde summarized by these authors allow generation of the following correlation expressions for aqueous aldehydes, based on the assumption that such correlations are parallel to those for other homologous series of organic compounds (Schulte and Shock, 1993),

$$\bar{S}^\circ = 6.7\,\bar{n} + 28.9 \tag{37}$$

and

$$\bar{C}_P^\circ = 21.2\,\bar{n} - 7.5. \tag{38}$$

The difference between the intercept value in eq (37) for aldehydes and that for carboxylic acids (from eq 14) is 0.4 cal mol^{-1} K^{-1}, which, as expected, is considerably less than that between alkanes and alcohols obtained above. Assuming that this difference is a close estimate for the transformation of monocarboxylic acids to hydroxyacids yields

$$\bar{S}^\circ = 6.7\,\bar{n} + 29.7 \tag{39}$$

from eq (14) which was used in this study to estimate values of $\bar{S}^\circ$ for hydroxyacids. Because values of thermodynamic properties of dissociation tend to reach a constant value with increasing $\bar{n}$, it was assumed that

$\Delta\bar{S}^\circ_D$ for lactic acid from table 9 is a reasonable estimate of this constant and corresponds to the offset between correlations of $\bar{S}^\circ$ versus $\bar{n}$ for hydroxyacids and acid anions. As a result, the following expression can be used to estimate values of $\bar{S}^\circ$ for hydroxyacid anions

$$\bar{S}^\circ = 6.7\,\bar{n} + 11.8. \tag{40}$$

The values of $\bar{S}^\circ$ from eq (39) together with values of S° of the elements from Cox, Wagman, and Medvedev (1989) and values of $\Delta\bar{H}^\circ_f$ from table 8 or estimated with eq (34) were used in this study to calculate values of $\Delta\bar{G}^\circ_f$ for hydroxyacids.

Comparison of eqs (6) and (38) demonstrates that the difference in intercept values of the $\bar{C}^\circ_P$ versus $\bar{n}$ correlations for aldehydes and carboxylic acids is 5.3 cal mol^{-1} K^{-1}. Once again, assuming that this difference is a reasonable approximation for the offset between carboxylic acid and hydroxyacid correlations, the following expression is obtained from eq (6)

$$\bar{C}^\circ_P = 21.2\,\bar{n} + 3.1, \tag{41}$$

which was used in this study to estimate values of $\bar{C}^\circ_P$ for hydroxyacids. Estimates for the corresponding acid anions were made from

$$\bar{C}^\circ_P = 21.2\,\bar{n} - 36.9 \tag{42}$$

after taking into account the values of $\Delta\bar{C}^\circ_{P,D}$ for glycolic and lactic acids shown in table 9 and assuming that the value for lactic acid more accurately represents the constant value approached by the higher homologue for which experimental data are lacking. Values of $\bar{V}^\circ$, $\bar{C}^\circ_P$, $\bar{S}^\circ$, $\Delta\bar{H}^\circ_f$, and $\Delta\bar{G}^\circ_f$ for hydroxyacids obtained as described above were used together with values of dissociation properties listed in table 9 to calculate the corresponding properties of the acid anions. These data are listed in table 10, together with equation of state parameters estimated as described in the next section.

Regression and prediction of equation of state parameters.—Apparent partial molal volumes of aqueous hydroxyacids and sodium salts of the corresponding anions were measured at 25°, 30°, and 35°C by Høiland and Vikingstad (1975) who extracted standard partial molal volumes from their experimental results. These data cover a narrow range of temperature but can nevertheless be regressed for values of σ and ξ after evaluating $\Delta\bar{V}^\circ_s$. Calculating solvation contributions requires values of ω and ω_e which were estimated in this study from eqs (A-26), (A-27), and (22) using the values of $\bar{S}^\circ$ estimated as described above and listed in table 10. Values of $\Delta\bar{V}^\circ_n$ evaluated from the $\bar{V}^\circ$ data given by Høiland and Vikingstad (1975) are plotted against $1/(T - \theta)$ in figure 15. The resulting values of $\bar{V}^\circ$, $\bar{V}^\circ_n$, σ, and ξ at 25°C and 1 bar are listed in table 11. These data were used together with the equations summarized above to esti-

TABLE 10

Summary of standard partial molal thermodynamic data at 25°C and 1 bar for aqueous hydroxyacid species adopted in this study, together with equation of state parameters required to calculate the corresponding properties at high temperatures and pressures. Unless otherwise indicated, thermodynamic data in this table correspond to selected values from table 8, and parameters were estimated with the revised correlation algorithm discussed in the text

Species	$\Delta\overline{G}_f^{\circ a}$	$\Delta\overline{H}_f^{\circ a}$	$\overline{S}^{\circ b}$	$\overline{C}_p^{\circ b}$	$\overline{V}^{\circ c}$	$a_1^d \times 10^{-2}$	$a_2^a \times 10^{-2}$	a_3^e	$a_4^f \times 10^{-4}$	c_1^b	$c_2^f \times 10^{-4}$	$\omega_e^a \times 10^{-5}$
glycolic acid	-126400.^{n}	-154890.	43.1^g	45.5^l	51.75	8.7445	12.1496	4.0222	-3.2812	43.6669	-0.4655	-0.3017
lactic acid	-127800.^{n}	-164000.	49.8^g	66.7^l	69.38	11.1720	17.2432	3.8083	-3.4917	61.0199	1.6290	-0.2572
2hydroxybutanoic acid	-125750.^{n}	-169670.^{k}	56.5^g	87.9^l	85.45	13.3861	22.2951	2.5821	-3.7006	78.3729	3.7235	-0.2128
2-hydroxypentanoic acid	-123700.^{n}	-175340.^{k}	63.2^g	109.1^l	100.47	15.4564	27.0371	1.3904	-3.8966	95.7257	5.8181	-0.1684
2-hydroxyhexanoic acid	-121650.^{n}	-181010.^{k}	69.9^g	130.3^l	117.26	17.7690	33.3994	-2.6456	-4.1596	113.0787	7.9126	-0.1240
2-hydroxyheptanoic acid	-119600.^{n}	-186680.^{k}	76.6^g	151.5^l	132.1^i	19.8147	38.1868	-4.0817	-4.3375	130.4315	10.0072	-0.0795
2-hydroxyoctanoic acid	-117550.^{n}	-192350.^{k}	83.3^g	172.7^l	147.9^i	21.9918	43.1173	-5.1928	-4.5614	147.7843	12.1018	-0.0351
2-hydroxynonanoic acid	-115520.^{n}	-198020.^{k}	90.0^g	193.9^l	163.7^i	24.1688	48.0543	-6.3200	-4.7655	165.1372	14.1963	0.0093
2-hydroxydecanoic acid	-113480.^{n}	-203690.^{k}	96.7^g	215.1^l	179.5^i	26.3459	52.9848	-7.4315	-4.9693	182.4900	16.2909	0.0537
glycolate	-121170.^{p}	-154700.^{r}	26.2^h	6.5^m	39.85	7.6349	11.0570	0.9834	-3.2360	26.0463	-4.0271	1.2334
lactate	-122530.^{p}	-164070.^{r}	31.9^h	26.7^m	56.25	9.8498	12.8244	8.0990	-3.3091	44.9518	-3.7823	1.1469
2-hydroxybutanoate	-120550.^{p}	-169810.^{r}	38.6h	47.9^m	71.61	11.9172	20.2720	0.0242	-3.6169	64.6903	-3.5254	1.0449
2-hydroxypentanoate	-118800.^{p}	-175770.^{r}	45.3h	69.1^m	86.71	13.9490	24.1569	0.8050	-3.7775	84.4263	-3.2684	0.9427
2-hydroxyhexanoate	-116550.^{q}	-181240.^{r}	52.0^h	90.3^m	103.33	16.1891	30.4279	-3.3776	-4.0368	104.1738	-3.0115	0.8417
2-hydroxyheptanoate	-114500.^{q}	-186900.^{r}	58.7^h	111.5^m	118.6^j	18.2444	34.6247	-3.2651	-4.2103	123.9167	-2.7545	0.7402
2-hydroxyoctanoate	-112450.^{q}	-192570.^{r}	65.4^h	132.7^m	134.4^j	20.3721	39.4474	-4.3607	-4.4097	143.6592	-2.4976	0.6387
2-hydroxynonanoate	-110420.^{q}	-198250.^{r}	72.1^h	153.9^m	150.2^j	22.4999	44.2700	-5.4567	-4.6090	163.4021	-2.2406	0.5372
2-hydroxydecanoate	-108380.^{q}	-203930.^{r}	78.8^h	175.1^m	166.0^j	24.6277	49.0925	-6.5525	-4.8084	183.1446	-1.9837	0.4356

[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] estimated with eq (39), [h] estimated with eq (40), [i] estimated with eq (32), [j] estimated with eq (33), [k] estimated with eq (36), [l] estimated with eq (41), [m] estimated with eq (42), [n] calculated from $\Delta\overline{H}_f^\circ$ and $\overline{S}^\circ$ in table, together with S° of the elements from Cox, Wagman, and Medvedev (1989), [p] calculated from the value of $\Delta\overline{G}_f^\circ$ for the acid in the table and the selected value of $\Delta\overline{G}_D^\circ$ from table 9, [q] estimated from the value of $\Delta\overline{G}_f^\circ$ for the acid in the table and the assumption that $\Delta\overline{G}_D^\circ$ is 5100 cal mol^{-1} (see text), [r] calculated from $\Delta\overline{G}_f^\circ$ and $\overline{S}^\circ$ in the table, together with S° of the elements from Cox, Wagman, and Medvedev (1989).

mate the volumetric equation of state parameters in table 10. Values of σ and $\Delta\overline{V}^\circ_n$ are plotted in figure 16 where it can be seen that they are in close agreement with the correlation line obtained from the data shown in figure 8 and given by eq (23). Encouraged by this agreement, the $\overline{C}^\circ_P$ versus c_2 correlations for neutral aqueous organic compounds and organic anions shown in figure 9 and given by eqs (28) and (29) were also used in this study.

Estimation of equilibrium constants.—Data and parameters from table 10, together with eqs (30), (31), (A-25), and (A-37) allow estimation of log K values for hydroxyacid dissociation reactions at high temperatures and pressures. Predictions of this type are given in table 12 at several temperatures and pressures of geochemical interest. Comparisons of predicted and experimental log K values can be made for glycolic and lactic acids as shown in figure 17. Agreement between predictions and experiments is generally very close for these acids, but it should be kept in mind that the narrow range of temperature over which experimental log K values are available does not permit a thoroughly rigorous test of the data and parameters in table 10 or the estimation procedures used to obtain a vast majority of them.

CONCLUDING REMARKS

Equations, data, and parameters outlined above allow prediction of thermodynamic properties of many aqueous organic acids and anions. Comparisons between predictions and experimental data at elevated temperatures and pressures show close agreement which suggests that the values of log K in tables 7 and 12 can be used with considerable confidence in studies of geochemical processes involving organic acids. In addition, it should be possible to develop estimation procedures like those described here to enable the inclusion of many more aqueous organic species in geochemical calculations. The thermodynamic properties of aqueous organic acids summarized above provide a quantitative foundation for a realistic consideration of the impact of metal-organic complexes on the transport of metals and dissolved organic carbon at the temperatures and pressures of geochemical processes (Shock and Koretsky, 1993, 1995; Koretsky and Shock, 1993). These same data can be used to examine decarboxylation and oxidation/reduction reactions which should help reveal the reasons for the observed ratios of organic acids in oil-field brines and hydrothermal solutions (Shock, 1988, 1989, 1990; Helgeson and Shock, 1988; Helgeson and others, 1993) and provide the means to study the origin of organic acids through abiotic reactions (Shock, 1990, 1992a; Schulte and Shock, 1993, 1995) as well as during organic matter alteration and petroleum generation both in natural environments and in the laboratory. These predictions should also prove useful in evaluating geochemical constraints on the bioenergetics of microorganisms living at elevated temperatures and pressures. Computer files containing data and parameters listed in tables 4 and 10

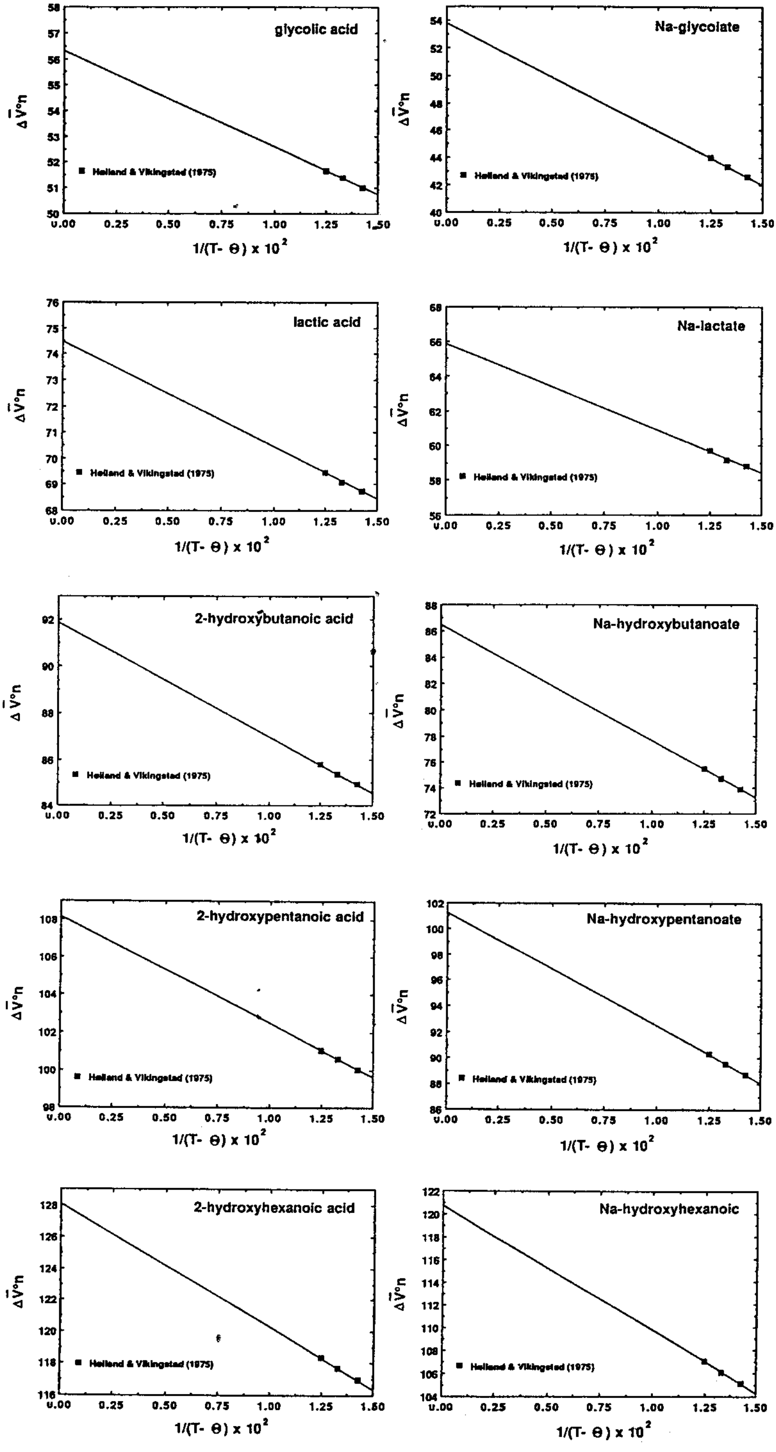


Fig. 15. Regression plots of $\Delta\overline{V}_n^\circ$ versus $1/(T - \Theta)$ for hydroxyacids and Na-hydroxyacid anion electrolytes. Symbols indicate data from Høiland and Vikingstad (1975), but lines represent regression results using eq (A-11).

TABLE 11

Volumetric data at 25°C and 1 bar for aqueous hydroxyacids, together with equation of state parameters obtained by regression

Species	$\bar{V}^{\circ a}$	$\Delta\bar{V}_n^{\circ a}$	σ^a	$\xi^b \times 10^{-2}$
glycolic	51.75	51.00	56.31	−3.72
glycolate	39.85	42.89	49.73	−4.79
lactic	69.38	68.75	74.48	−4.03
lactate	56.25	59.09	61.84	−1.95
2-hydroxybutanoic	85.45	84.92	91.87	−4.88
2-hydroxybutanoate	71.61	74.19	82.47	−5.80
2-hydroxypentanoic	100.47	100.05	108.16	−5.68
2-hydroxypentanoate	86.71	89.03	97.22	−5.74
2-hydroxyhexanoic	117.26	116.95	128.07	−7.80
2-hydroxyhexanoate	103.33	105.41	116.68	−7.92

[a] $cm^3 mol^{-1}$, [b] $cm^3 K mol^{-1}$.

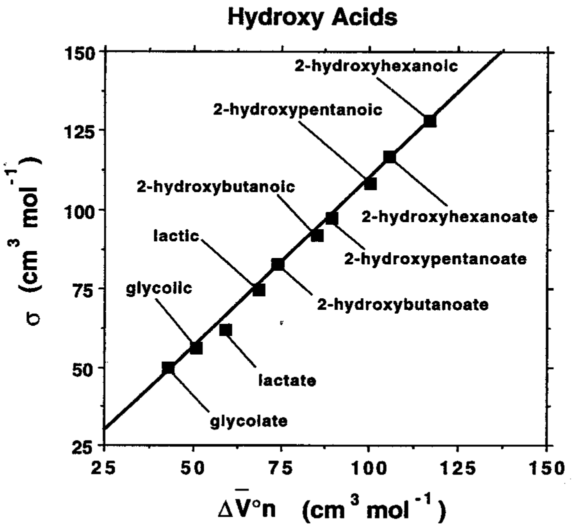


Fig. 16. Correlation of σ and $\Delta\bar{V}_n^\circ$ values at 25°C and 1 bar for hydroxyacids and anions taken from table 11. The correlation line shown is that obtained for a wide variety of aqueous species shown in figure (12) and corresponds to eq (23).

in a format which is consistent with the SUPCRT92 program (Johnson, Oelkers, and Helgeson, 1992) are available from this laboratory.

ACKNOWLEDGMENTS

The research described above was funded by NSF grants EAR-8803822 and EAR-9018468 and benefitted from discussions with Richard Kettler, Dimitri Sverjensky, Jan Amend, J. K. Böhlke, Julie Bell,

TABLE 12

Values of log K for hydroxyacid dissociation reactions at various temperatures (in °C) and P_{SAT}, 500 bars, 1000 bars, and 2000 bars, calculated with eqs (30), (31), (A-25), and (A-37) using data and parameters from table 10

P_{SAT}

Acid\Temperature °C	0.01	25	50	75	100	125	150	175	200	225	250	275	300	325	350
glycolic	-3.88	-3.83	-3.85	-3.91	-4.00	-4.12	-4.27	-4.43	-4.62	-4.83	-5.07	-5.35	-5.69	-6.14	-6.76
lactic	-3.90	-3.86	-3.89	-3.96	-4.07	-4.19	-4.34	-4.50	-4.68	-4.89	-5.11	-5.38	-5.70	-6.12	-6.70
2-hydroxybutanoic	-3.84	-3.81	-3.85	-3.92	-4.02	-4.14	-4.27	-4.43	-4.59	-4.78	-4.99	-5.23	-5.53	-5.91	-6.44
2-hydroxypentanoic	-3.60	-3.59	-3.64	-3.73	-3.83	-3.95	-4.09	-4.24	-4.40	-4.57	-4.77	-4.99	-5.26	-5.61	-6.09
2-hydroxyhexanoic	-3.76	-3.74	-3.78	-3.85	-3.94	-4.05	-4.17	-4.30	-4.43	-4.59	-4.76	-4.95	-5.18	-5.48	-5.91
2-hydroxyheptanoic	-3.76	-3.74	-3.78	-3.85	-3.93	-4.03	-4.14	-4.25	-4.38	-4.51	-4.66	-4.83	-5.02	-5.28	-5.64
2-hydroxyoctanoic	-3.77	-3.74	-3.78	-3.84	-3.92	-4.01	-4.11	-4.21	-4.32	-4.44	-4.56	-4.70	-4.87	-5.08	-5.36
2-hydroxynonanoic	-3.77	-3.74	-3.78	-3.84	-3.91	-4.00	-4.08	-4.17	-4.27	-4.36	-4.46	-4.58	-4.71	-4.87	-5.08
2-hydroxydecanoic	-3.77	-3.74	-3.78	-3.84	-3.91	-3.98	-4.06	-4.13	-4.21	-4.29	-4.37	-4.45	-4.54	-4.65	-4.79

500 Bars

Acid\Temperature °C	25	50	75	100	125	150	175	200	225	250	275	300	325	350	375	400
glycolic	-3.73	-3.76	-3.82	-3.91	-4.02	-4.15	-4.31	-4.47	-4.65	-4.86	-5.07	-5.32	-5.59	-5.91	-6.30	-6.78
lactic	-3.76	-3.78	-3.85	-3.95	-4.07	-4.20	-4.36	-4.52	-4.70	-4.89	-5.10	-5.34	-5.60	-5.90	-6.27	-6.73
2-hydroxybutanoic	-3.70	-3.74	-3.81	-3.91	-4.03	-4.16	-4.30	-4.45	-4.62	-4.80	-4.99	-5.20	-5.44	-5.71	-6.05	-6.48
2-hydroxypentanoic	-3.48	-3.53	-3.62	-3.72	-3.84	-3.97	-4.11	-4.26	-4.42	-4.59	-4.76	-4.96	-5.18	-5.43	-5.74	-6.13
2-hydroxyhexanoic	-3.62	-3.67	-3.74	-3.83	-3.94	-4.05	-4.18	-4.31	-4.44	-4.59	-4.74	-4.92	-5.10	-5.32	-5.59	-5.93
2-hydroxyheptanoic	-3.63	-3.67	-3.74	-3.83	-3.93	-4.03	-4.14	-4.26	-4.38	-4.51	-4.64	-4.79	-4.95	-5.14	-5.37	-5.66
2-hydroxyoctanoic	-3.63	-3.67	-3.74	-3.82	-3.91	-4.01	-4.11	-4.21	-4.32	-4.43	-4.54	-4.67	-4.80	-4.95	-5.14	-5.37
2-hydroxynonanoic	-3.63	-3.67	-3.74	-3.81	-3.90	-3.99	-4.07	-4.16	-4.25	-4.34	-4.44	-4.54	-4.65	-4.77	-4.91	-5.08
2-hydroxydecanoic	-3.63	-3.67	-3.73	-3.81	-3.88	-3.96	-4.04	-4.11	-4.19	-4.26	-4.34	-4.42	-4.49	-4.58	-4.67	-4.77

1000 Bars

Acid\Temperature °C	50	100	150	200	250	300	350	400	450	500	550	600
glycolic	-3.67	-3.82	-4.06	-4.35	-4.69	-5.08	-5.52	-6.05	-6.70	-7.47	-8.45	-9.57
lactic	-3.68	-3.85	-4.09	-4.39	-4.72	-5.10	-5.52	-6.02	-6.64	-7.38	-8.31	-9.37
2-hydroxybutanoic	-3.63	-3.81	-4.05	-4.33	-4.64	-4.99	-5.37	-5.83	-6.39	-7.07	-7.92	-8.90
2-hydroxypentanoic	-3.43	-3.63	-3.87	-4.15	-4.44	-4.76	-5.12	-5.53	-6.04	-6.66	-7.43	-8.32
2-hydroxyhexanoic	-3.56	-3.74	-3.96	-4.20	-4.45	-4.73	-5.04	-5.40	-5.85	-6.38	-7.06	-7.83
2-hydroxyheptanoic	-3.57	-3.73	-3.93	-4.15	-4.38	-4.63	-4.89	-5.20	-5.58	-6.03	-6.60	-7.26
2-hydroxyoctanoic	-3.57	-3.73	-3.92	-4.11	-4.31	-4.52	-4.75	-5.00	-5.31	-5.67	-6.13	-6.65
2-hydroxynonanoic	-3.57	-3.72	-3.90	-4.07	-4.24	-4.42	-4.60	-4.80	-5.03	-5.30	-5.63	-6.01
2-hydroxydecanoic	-3.57	-3.72	-3.88	-4.03	-4.17	-4.31	-4.45	-4.59	-4.75	-4.91	-5.11	-5.33

2000 Bars

Acid\Temperature °C	50	100	150	200	250	300	350	400	450	500	550	600	650	700	750
glycolic	-3.50	-3.66	-3.89	-4.17	-4.46	-4.79	-5.14	-5.52	-5.94	-6.38	-6.83	-7.31	-7.82	-8.35	-8.90
lactic	-3.51	-3.67	-3.90	-4.18	-4.48	-4.79	-5.13	-5.50	-5.90	-6.32	-6.75	-7.20	-7.68	-8.18	-8.70
2-hydroxybutanoic	-3.44	-3.64	-3.88	-4.14	-4.42	-4.71	-5.02	-5.35	-5.72	-6.10	-6.49	-6.90	-7.33	-7.78	-8.25
2-hydroxypentanoic	-3.24	-3.45	-3.70	-3.96	-4.23	-4.50	-4.79	-5.10	-5.43	-5.78	-6.12	-6.49	-6.88	-7.29	-7.71
2-hydroxyhexanoic	-3.37	-3.56	-3.78	-4.01	-4.25	-4.49	-4.74	-5.01	-5.30	-5.60	-5.90	-6.22	-6.56	-6.91	-7.27
2-hydroxyheptanoic	-3.38	-3.56	-3.77	-3.98	-4.19	-4.41	-4.63	-4.86	-5.10	-5.36	-5.61	-5.88	-6.17	-6.47	-6.77
2-hydroxyoctanoic	-3.38	-3.56	-3.75	-3.95	-4.14	-4.32	-4.51	-4.70	-4.91	-5.12	-5.33	-5.55	-5.78	-6.02	-6.26
2-hydroxynonanoic	-3.38	-3.55	-3.74	-3.91	-4.08	-4.24	-4.39	-4.55	-4.71	-4.88	-5.04	-5.20	-5.38	-5.56	-5.74
2-hydroxydecanoic	-3.38	-3.55	-3.72	-3.88	-4.02	-4.15	-4.28	-4.40	-4.52	-4.63	-4.74	-4.86	-4.97	-5.09	-5.21

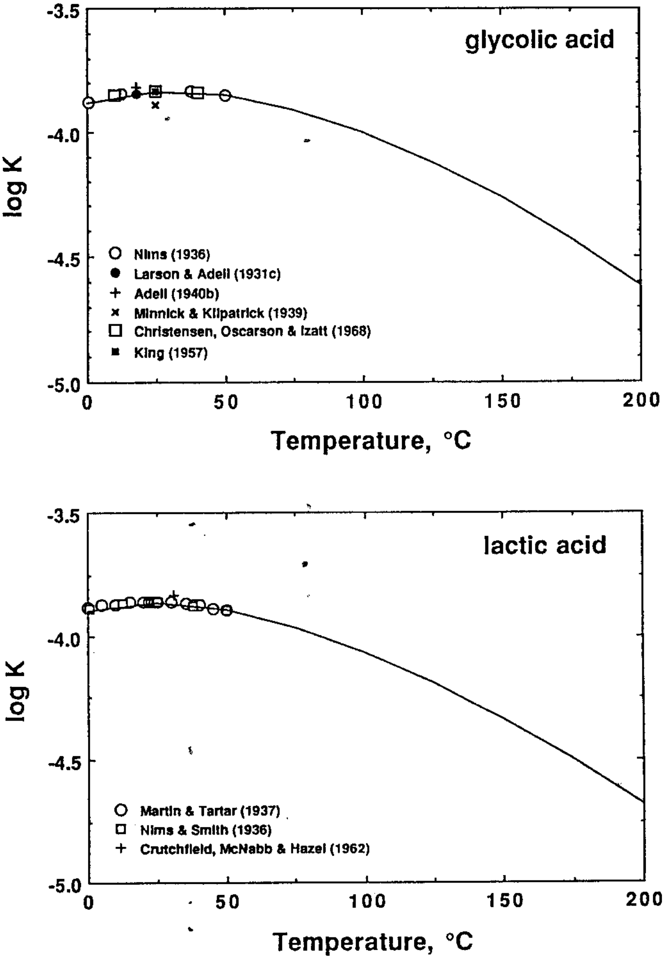


Fig. 17. Plots of log K against temperature for the dissociation of glycolic and lactic acid at P_{SAT}. Symbols represent experimental data from the references listed in the figure, but the curves represent predictions made with the revised-HKF equations of state using data and parameters from table 10.

Laura Crossey, Mike Lewan, Bert Fisher, David Sassani, Mitch Schulte, Tom McCollom, David Wesolowski, Wendy Harrison, Robert Wood, and Harold Helgeson. Thanks are due to Richard Kettler and David Wesolowski for sharing experimental data in advance of publication, to Jan Amend for pointing out the diols and diamine data, to Wendy Harrison for a constructive and helpful review, and to Danny Rye for his patience with the review process. Technical assistance from Carla Koretsky, Patty DuBois, Michelle Morgan, Dee Becker, Rebecca Lloyd, Jennifer Barmann, and Bill Winston is greatly appreciated.

APPENDIX I

Standard state conventions

The standard state convention for aqueous ions, electrolytes, and neutral species adopted in the present study is one of unit activity of the aqueous species 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. Any standard partial molal property of the **kth** aqueous electrolyte ($\overline{\Xi}^{\circ}_{k}$) is related to the corresponding absolute standard partial molal properties of its constituent ions by

$$\overline{\Xi}^{\circ}_{k} = \sum_{j} \nu_{j,k}\overline{\Xi}^{\circ abs}_{j} \tag{A-1}$$

where the subscripts k and j refer to the electrolyte and ion, respectively. The conventional standard partial molal properties of the **jth** ion are defined by

$$\overline{\Xi}^{\circ}_{j} \equiv \overline{\Xi}^{\circ abs}_{j} - z_j\overline{\Xi}^{\circ abs}_{H^+} \tag{A-2}$$

where $\overline{\Xi}^{\circ abs}_{H^+}$ refers to the absolute standard partial molal property of the hydrogen ion. As a consequence, all conventional standard partial molal properties of H^+ are equal to 0.0 at all pressures and temperatures. It follows from eqs (A-1) and (A-2) and the requirement for electrical neutrality of an aqueous electrolyte that

$$\overline{\Xi}^{\circ}_{k} = \sum_{j} \nu_{j,k}\overline{\Xi}^{\circ}_{j}. \tag{A-3}$$

Summary of the Revised-HKF Equation of State

The standard partial molal properties of aqueous species are expressed in the revised-HKF equation of state in terms of structural and solvation contributions. A general statement of this summation can be expressed

$$\overline{\Xi}^{\circ}_{j} = \Delta\overline{\Xi}^{\circ}_{n} + \Delta\overline{\Xi}^{\circ}_{s} \tag{A-4}$$

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

$$\begin{aligned}\overline{V}^{\circ} &= \overline{V}^{\circ}_{n} + \overline{V}^{\circ}_{s}\\ &= \sigma + \frac{\xi}{T-\theta} - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T\\ &= a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P}\right)\left(\frac{1}{T-\theta}\right) - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T,\end{aligned} \tag{A-5}$$

and

$$\begin{aligned}\overline{C}^{\circ}_{P} &= \Delta\overline{C}^{\circ}_{P,n} + \Delta\overline{C}^{\circ}_{P,s}\\ &= c_1 + \frac{c_2}{(T-\theta)^2} - \left(\frac{2T}{(T-\theta)^3}\right)\left(a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right)\\ &\quad + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P,\end{aligned} \tag{A-6}$$

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, Pr signifies the reference pressure of 1 bar, and Q, Y, and X indicate the Born functions defined by

$$Q \equiv \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T, \tag{A-7}$$

$$Y \equiv \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial T}\right)_P, \tag{A-8}$$

and

$$X \equiv \left(\frac{\partial Y}{\partial T}\right)_P = \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P^2\right], \tag{A-9}$$

where ϵ stands for the dielectric constant of H_2O. The following identities are consistent with eqs (A-5) and (A-6)

$$\Delta\overline{V}^\circ_s = -\omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial \omega}{\partial T}\right)_T, \tag{A-10}$$

$$\Delta\overline{V}^\circ_n = \sigma + \frac{\xi}{T - \theta}, \tag{A-11}$$

$$\sigma = a_1 + \frac{a_2}{\Psi + P}, \tag{A-12}$$

$$\xi = a_3 + \frac{a_4}{\Psi + P}, \tag{A-13}$$

$$\Delta\overline{C}^\circ_{P,s} = -\omega TX + 2TY\left(\frac{\partial \omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P, \tag{A-14}$$

and

$$\Delta\overline{C}^\circ_{P,n} = c_1 + \frac{c_2}{(T - \theta)^2} - \left(\frac{2T}{(T - \theta)^3}\right)\left(a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right) \tag{A-15}$$

which reduces for P = Pr to

$$\Delta\overline{C}^\circ_{P,n} = c_1 + \frac{c_2}{(T - \theta)^2}. \tag{A-16}$$

Eq (A-16) can be used at P_{SAT} to temperature of ~200°C without introducing substantial error (Shock and Helgeson, 1988, 1990; Shock, Helgeson, and Sverjensky, 1989). In the case of neutral aqueous species, eqs (A-10) and (A-14) reduce to

$$\Delta\overline{V}^\circ_s = -\omega_e Q, \tag{A-17}$$

$$\Delta\overline{C}^\circ_{P,s} = \omega_e TX. \tag{A-18}$$

Integration of eq (A-6) with respect to temperature yields

$$\bar{S}^{\circ} = \bar{S}^{\circ}_{Pr,Tr} + c_1 \ln(T/Tr) - \frac{c_2}{\theta}\left[\left(\frac{1}{T-\theta}\right) - \left(\frac{1}{Tr-\theta}\right) + \frac{1}{\theta}\ln\left(\frac{Tr(T-\theta)}{T(Tr-\theta)}\right)\right]$$
$$+ \left(\frac{1}{T-\theta}\right)^2\left(a_3(P-Pr) + a_4\ln\left(\frac{\Psi+P}{\Psi+Pr}\right)\right)$$
$$+ \omega Y - \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{Pr,Tr}Y_{Pr,Tr}, \tag{A-19}$$

where Tr 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, Kirkham, and Flowers, 1981; Tanger and Helgeson, 1988)

$$\Delta\bar{G}^{\circ} \equiv \Delta\bar{G}^{\circ}_f + (\bar{G}^{\circ}_{P,T} - \bar{G}^{\circ}_{Pr,Tr}) \tag{A-20}$$

$$\Delta\bar{H}^{\circ} \equiv \Delta\bar{H}^{\circ}_f + (\bar{H}^{\circ}_{P,T} - \bar{H}^{\circ}_{Pr,Tr}) \tag{A-21}$$

where $\Delta\bar{G}^{\circ}_f$ and $\Delta\bar{H}^{\circ}_f$ stand for the conventional standard partial molal Gibbs free energy and enthalpy of formation of the species from elements 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 eqs (A-5), (A-6), (A-20), and (A-21) together with

$$\bar{H}^{\circ}_{P,T} - \bar{H}^{\circ}_{Pr,Tr} = \int_{Tr}^{T}\bar{C}^{\circ}_{Pr}\,dT + \int_{Pr}^{P}\left(\bar{V}^{\circ} - T\left(\frac{\partial\bar{V}^{\circ}}{\partial T}\right)_P\right)_T dP, \tag{A-22}$$

$$\bar{G}^{\circ}_{P,T} - \bar{G}^{\circ}_{Pr,Tr} = -\bar{S}^{\circ}_{Pr,Tr}(T-Tr) + \int_{Tr}^{T}\bar{C}^{\circ}_{Pr}\,dT - T\int_{Tr}^{T}\bar{C}^{\circ}_{Pr}\,d\ln T + \int_{Pr}^{P}\bar{V}^{\circ}_T\,dP, \tag{A-23}$$

and the partial isobaric temperature derivative of eq (A-5), that we can write

$$\Delta\bar{H}^{\circ} = \Delta\bar{H}^{\circ}_f + c_1(T-Tr) - c_2\left[\left(\frac{1}{T-\theta}\right) - \left(\frac{1}{Tr-\theta}\right)\right] + a_1(P-Pr)$$
$$+ a_2\ln\left(\frac{\Psi+P}{\Psi+Pr}\right) + \left(\frac{2T-\theta}{(T-\theta)^2}\right)\left(a_3(P-Pr) + a_4\ln\left(\frac{\Psi+P}{\Psi+Pr}\right)\right)$$
$$+ \omega\left(\frac{1}{\epsilon} - 1\right) + \omega TY - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{Pr,Tr}\left(\frac{1}{\epsilon_{Pr,Tr}} - 1\right)$$
$$-\omega_{Pr,Tr}TrY_{Pr,Tr} \tag{A-24}$$

and

$$
\begin{aligned}
\Delta\bar{G}^\circ = {} & \Delta\bar{G}_f^\circ - \bar{S}^\circ_{Pr,Tr}(T - Tr) - c_1\left(T \ln\left(\frac{T}{Tr}\right) - T + Tr\right) \\
& - c_2\left(\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{Tr - \theta}\right)\right]\left(\frac{\theta - T}{\theta}\right) - \frac{T}{\theta^2} \ln\left(\frac{Tr(T - \theta)}{T(Tr - \theta)}\right)\right) \\
& + a_1(P - Pr) + a_2 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right) \\
& + \left(\frac{1}{T - \theta}\right)\left[a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right] \\
& + \omega\left(\frac{1}{\epsilon} - 1\right) - \omega_{Pr,Tr}\left(\frac{1}{\epsilon_{Pr,Tr}} - 1\right) - \omega_{Pr,Tr}Y_{Pr,Tr}(T - Tr). \qquad \text{(A-25)}
\end{aligned}
$$

The conventional Born coefficient (ω) which appears in eqs (A-5), (A-6), (A-10), (A-14), (A-19), (A-24), and (A-25) is defined for the **jth** ionic species by

$$\omega \equiv \omega_j^{abs} - Z_j\omega_{H^+}^{abs}, \qquad \text{(A-26)}$$

where $\omega_{H^+}^{abs}$ denotes the absolute Born coefficient of the hydrogen ion, which is taken to be 0.5387×10^5 cal mol^{-1} at 25°C and 1 bar (Helgeson and Kirkham, 1976), and

$$\omega_j^{abs} = \frac{\eta Z_j^2}{r_{e,j}}, \qquad \text{(A-27)}$$

where $\eta = 1.66027 \times 10^5$ (Å, cal, mol^{-1}), Z_j stands for the charge on the ion, and $r_{e,j}$ designates the effective electrostatic radius of the **jth** aqueous ion given by (Tanger and Helgeson, 1988; Shock and others, 1992)

$$r_{e,j} = r_{x,j} + |z_j|(k_z + g), \qquad \text{(A-28)}$$

where $r_{x,j}$ stands for the crystallographic radius of the ions, k_z represents a constant equal to 0.0 for anions and 0.94 for cations, and g denotes a temperature and pressure dependent solvent function. Values of the g function have been regressed from standard partial molal volume and heat capacity data for the electrolyte NaCl (Tanger and Helgeson, 1988) and from supercritical equilibrium constants (Shock and others 1992) for the reaction

$$NaCl^\circ \leftrightarrow Na^+ + Cl^- \qquad \text{(A-29)}$$

where NaCl° represents the neutral, associated complex species. Available expressions for the g function allow calculation of conventional Born coefficients and their partial derivatives to 1000°C and 5 kb (Shock and others, 1992).

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, Helgeson, and Sverjensky, 1989)

$$\omega_{e,n} = \frac{\eta Z_{e,n}^2}{r_{e,n}} \qquad \text{(A-30)}$$

where $Z_{e,n}$ refers to the effective charge of the **nth** neutral aqueous species. 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, Helgeson, and Sverjensky, 1989; Shock and Helgeson, 1990; Sverjensky, Shock, and Helgeson 1995; Shock and others, 1992; Shock, 1995; and the present study). It follows that the revised-HKF expressions for the solvation contributions to the standard partial molal volumes and heat capacities are given by

$$\Delta \overline{V}^{\circ}_{s} = -\omega_e Q \tag{A-31}$$

$$\Delta \overline{C}^{\circ}_{P,s} = \omega_e TX. \tag{A-32}$$

As a consequence, the revised-HFK expressions for the standard partial molal properties of neutral aqueous species can be expressed as (Shock, Helgeson, and Sverjensky, 1989)

$$\overline{V}^{\circ} = a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P}\right)\left(\frac{1}{T - \theta}\right) - \omega_c Q, \tag{A-33}$$

$$\overline{C}^{\circ}_{P} = c_1 + \frac{c_2}{(T - \theta)^2} - \left(\frac{2T}{(T - \theta)^3}\right)\left(a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right) + \omega_c TX, \tag{A-34}$$

$$\begin{aligned}\overline{S}^{\circ} = {} & \overline{S}^{\circ}_{Pr,Tr} + c_1 \ln (T/Tr) - \frac{c_2}{\theta}\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{Tr - \theta}\right) + \frac{1}{\theta} \ln\left(\frac{Tr(T - \theta)}{T(Tr - \theta)}\right)\right] \\ & + \left(\frac{1}{T - \theta}\right)^2\left(a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right) + \omega_e(Y - Y_{Pr,Tr}),\end{aligned} \tag{A-35}$$

$$\begin{aligned}\Delta \overline{H}^{\circ} = {} & \Delta \overline{H}^{\circ}_{f} + c_1(T - Tr) - c_2\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{Tr - \theta}\right)\right] + a_1(P - Pr) \\ & + a_2 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right) + \left(\frac{2T - \theta}{(T - \theta)^2}\right)\left(a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right) \\ & + \omega_e\left(TY - TrY_{Pr,Tr} + \left(\frac{1}{\epsilon} - 1\right) - \left(\frac{1}{\epsilon_{Pr,Tr}} - 1\right)\right),\end{aligned} \tag{A-36}$$

and

$$\begin{aligned}\Delta \overline{G}^{\circ} = {} & \overline{G}^{\circ}_{f} - \overline{S}^{\circ}_{Pr,Tr}(T - Tr) - c_1\left(T \ln\left(\frac{T}{Tr}\right) - T + Tr\right) \\ & - c_2\left(\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{Tr - \theta}\right)\right]\left(\frac{\theta - T}{\theta}\right) - \frac{T}{\theta^2} \ln\left(\frac{Tr(T - \theta)}{T(Tr - \theta)}\right)\right) \\ & + a_1(P - Pr) + a_2 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right) \\ & + \left(\frac{1}{T - \theta}\right)\left[a_3(P - Pr) + a_4 \ln\left(\frac{\Psi + P}{\Psi + Pr}\right)\right] \\ & + \omega_e\left(Y_{Pr,Tr}(T - Tr) + \left(\frac{1}{\epsilon} - 1\right) - \left(\frac{1}{\epsilon_{Pr,Tr}} - 1\right)\right).\end{aligned} \tag{A-37}$$

REFERENCES

Abercrombie, H. J., 1991, Reservoir processes in steam-assisted recovery of bitumen, Leming pilot, Cold Lake, Alberta, Canada; compositions, mixing and sources of co-produced waters: Applied Geochemistry, v. 6, p. 495–508.

Abichandani, C. T., and Jatkar, S. K. K., 1938, Dissociation constants of ortho-, meta- and para-hydroxy benzoic acids, gallic acid, catechol, resorcinol, hydroquinone, pyrogallol and phloroglucinol: Journal of the Indian Institute of Science, v. A21, p. 417–441.

——— 1941, Dissociation constants of isomeric halogenophenols: Journal of the Indian Institute of Science, v. A23, p. 99–130.

Abraham, M. H., 1984, Thermodynamics of solution of homologous series of solutes in water: Journal of the Chemical Society, Faraday Transactions I, v. 80, p. 153–181.

Ackermann, T., and Schreiner, F., 1958, Molwärmen and Entropien einiger Fettsäuren and ihrer Anionen in wässriger Lösung: Zeitschrift für Electrochemie, v. 62, p. 1143–1151.

Adell, B., 1940a, Uber die elektrolytische Dissoziation von Dicarbonsäuren in Wasser und in wasserigen Alkalichloridlosungen: Zeitschrift für Physikalische Chemie, v. 185, p. 161–206.

——— 1940b, Uber die Dissoziation der Essig-, Glykol- und Malonsaure in Glycerin-wasser-gemischen: Zeitschrift für Physikalische Chemie, v. 186, p. 27–53.

Allen, H. L., 1968, Acetate in fresh water: natural substrate concentrations determined by dilution bioassay: Ecology, v. 49, p. 346–349.

Allred, G. C., and Woolley, E. M., 1981, Heat capacities of aqueous acetic acid, sodium acetate, ammonia, and ammonium chloride at 283.15, 298.15, and 313.15 K: $\Delta \bar{C}^{\circ}_{p}$ for ionization of acetic acid and for dissociation of ammonium ion: Journal of Chemical Thermodynamics, v. 13, p. 155–164.

Andreae, M. O., Talbot, R. W., Andreae, T. W., and Harris, R. C., 1988, Formic and acetic acid over the central Amazon region, Brazil. 1. Dry season: Journal of Geophysical Research, v. 93, p. 1616–1624.

Andreae, M. O., Talbot, R. W., and Li, S. M., 1987, Atmospheric measurement of pyruvic acid: Journal of Geophysical Research, v. 92, p. 6635–6641.

Antweiler, R. C., and Drever, J. I., 1983, The weathering of a late Tertiary volcanic ash: importance of organic solutes: Geochimica et Cosmochimica Acta, v. 47, p. 623–629.

Apelblat, A., 1986, Enthalpy of solution of oxalic, succinic, adipic, maleic, malic, tartaric, and citric acids, oxalic acid dihydrate, and citric acid monohydrate in water at 298.15 K: Journal of Chemical Thermodynamics, v. 18, p. 351–357.

——— 1990, Enthalpies of solution of malonic, glutaric, ascorbic, and DL-aspartic acids in water and of fumaric acid in 0.1 mol dm^{-3} HCl: Journal of Chemical Thermodynamics, v. 22, p. 253–256.

Apelblat, A., and Manzurola, E., 1989, Solubility of ascorbic, 2-furancarboxylic, glutaric, pimelic, salicylic, and o-phthalic acid in water from 279.15 to 342.15 K and apparent molar volumes of ascorbic, glutaric, and pimelic acids in water at 298.15 K: Journal of Chemical Thermodynamics, v. 21, p. 1005–1008.

——— 1990, Solubility of suberic, azelaic, levulinic, glycolic, and diglycolic acids in water from 278.25 K to 361.35 K: Journal of Chemical Thermodynamics, v. 22, p. 289–292.

Arnett, E. M., Small, L. E., Oancea, D., and Johnston, D., 1976, Heats of ionization of some phenols and benzoic acids in dimethyl sulfoxide. Heats of solvation of oxy-anions in dimethyl sulfoxide and water: Journal of the American Chemical Society, v. 98, p. 7346–7350.

Atkinson, R., and Lloyd, A. C., 1984, Evaluation of kinetic and mechanistic data for modeling of photochemical smog: Journal of Physical and Chemical Reference Data, v. 13, p. 315–444.

Backlund, S., Eriksson, F., Friman, R., Sjöblom, J., and Thylin, B., 1981, Thermodynamic excess quantities in aqueous solutions of short-chain ionic surfactants: Acta Chemica Scandinavica, v. 35A, p. 521–528.

Baker, J. W., Dippy, J. F. J., and Page, J. E., 1937, The dissociation constants of alkyl-substituted benzoic and phenylacetic acids: Journal of the Chemical Society, v. 1937, p. 1774–1779.

Banerjee, S. N., Sen Gupta, A. K., and Siddhanta, S. K., 1958, Some aliphatic monocarboxylate complexes of bivalent mono-acetato complex: Journal of the Indian Chemical Society, v. 35, p. 269–278.

Barcelona, M. J., 1980, Dissolved organic carbon and volatile fatty acids in marine sediment pore waters: Geochimica et Cosmochimica Acta, v. 44, p. 1977–1984.

Barcelona, M. J., Lijestrand, H. M., and Morgan, J. J., 1980, Determination of low molecular weight volatile fatty acids in aqueous samples: Analytical Chemistry, v. 52, p. 321–325.

Barth, T., 1987a, Quantitative determination of volatile carboxylic acid in formation waters by isotachophoresis: Analytical Chemistry, v. 59, p. 2232–2237.

——— 1987b, Multivariate analysis of aqueous organic acid concentrations and geological properties of North Sea reservoirs: Chemometrics and Intelligent Laboratory Systems, v. 2, p. 155–160.

——— 1991, Organic acids and inorganic ions in waters from petroleum reservoirs, Norwegian continental shelf: a multivariate statistical analysis and comparison with American reservoir formation waters: Applied Geochemistry, v. 6, p. 1–15.

Barth, T., and Bjorlykke, K., 1993, Organic acids from source rock maturation: generation potential, transport mechanisms, and relevance for mineral diagenesis: Applied Geochemistry, v. 8, p. 325–337.

Barth, T., Borgund, A. E., and Hopland, A. L., 1989, Generation of organic compounds by hydrous pyrolysis of Kimmeridge oil shale-Bulk results and activation energy calculations: Organic Geochemistry, v. 14, p. 69–76.

Barth, T., Borgund, A. E., Hopland, A. L., and Graue, A., 1987, Volatile organic acids produced during kerogen maturation-amounts, composition and role in migration of oil: Advances in Organic Geochemistry, v. 13, p. 461–465.

Basaran, B., Avsar, E., Erim, F. B., and Göçmen, A., 1991, Thermodynamics of benzoate complexes of cobalt(II), nickel(II) and manganese(II) in aqueous solution: Thermochimica Acta, v. 186, p. 145–151.

Bates, R. G., 1951, Determination of dissociation constants in a mixture of two weak acids by electromotive force measurements: Journal of the American Chemical Society, v. 73, p. 2259–2261.

Bates, R. G., and Canham, R. G., 1951, Resolution of the dissociation constants of d-tartaric acid from 0° to 50°C: Journal of Research of the National Bureau of Standards, v. 47, p. 343–348.

Bates, R. G., and Pinching, G. D., 1949, Resolution of the dissociation constants of citric acid at 0 to 50°, and determination of certain related thermodynamic functions: Journal of the American Chemical Society, v. 71, p. 1274–1283.

Bedrossian, A. A., and Cheh, H. Y., 1974, Effect of sodium acetate on the vapor-liquid equilibrium of the ethanol-water system: American Institute of Chemical Engineers Journal, v. 70, p. 102–109.

Belcher, D., 1938, The conductance and ionization constants of propionic and normal butyric acids in water at 25°: Journal of the American Chemical Society, v. 60, p. 2744–2747.

Bell, J. L., and Palmer, D. A., 1994, Experimental studies of organic acid decomposition, *in* Pittman, E. and Lewan, M., editors, Organic Acids in Geological Processes: Verlag-Springer New York, p. 226–269.

Bell, J. L., Wesolowski, D. J., and Palmer, D. A., 1993, The dissociation quotients of formic acid in sodium chloride solutions to 200°C: Journal of Solution Chemistry, v. 22, p. 125–136.

Bell, R. P., 1959, The Proton in Chemistry: Ithaca, New York, Cornell University Press, 310 p.

Bell, R. P., and Kuhn, A. T., 1963, Dissociation constants of some acids in deutrium oxide: Transactions of the Faraday Society, v. 59, p. 1789–1793.

Bell, R. P., and Waind, G. M., 1951, Reaction-kinetic investigations of incomplete dissociation of salts. Part III. The decomposition of nitramide in solutions of some metal salts of carboxylic acids: Journal of the Chemical Society, v. 1951, p. 2357–2362.

Bender, M., Heintz, A., and Lichtenthaler, R. N., 1991, Excess enthalpy of the system butyl acetate + butan-1-ol + acetic acid + water at 313 K and ambient pressure: Thermochimica Acta, v. 187, p. 79–94.

Bennett, P. C., Melcer, M. E., Siegel, D. I., and Hassett, J. P., 1988, The dissolution of quartz in dilute aqueous solutions of organic acids at 25°C: Geochimica et Cosmochimica Acta, v. 52, p. 1521–1530.

Benoit, R. L., Louis, C., and Frechette, M., 1991, Solution and ionization of some carboxylic acids in water and dimethyl sulfoxide: Thermochimica Acta, v. 176, p. 221–232.

Benson, S. W., 1976, Thermochemical Kinetics: New York, John Wiley and Sons, 320 p.

Bernardo-Gil, G., Esquível, M., and Ribeiro, A., 1990, Densities and refractive indices of pure organic acids as a function of temperature: Journal of Chemical and Engineering Data, v. 35, p. 202–204.

Bevan, J., and Savage, D., 1989, The effect of organic acids on the dissolution of K-feldspar under conditions relevant to burial diagenesis: Mineralogical Magazine, v. 53, p. 415–425.

Biedermann, G., and Molin, A., 1989, A new hydrogen electrode applied to the protolysis of acetic acid in potassium-acetate solutions: Acta Chemica Scandinavica, v. 43, p. 720–725.

Billen, G., Joiris, C., Wijnant, J., and Gillain, G., 1980, Concentration and microbiological utilization of small organic molecules in the Scheldt Estuary, the Belgian coastal zone of the North Sea and the English Channel: Estuarine, Coastal and Marine Science, v. 11, p. 279–294.

Bjerrum, J., Schwarzenbach, G., and Sillén, L. G., 1957, Stability Constants of Metal-ion Complexes, with Solubility Products of Inorganic Substances. Part I: Organic Ligands: London, The Chemical Society, 105 p.

Bjerrum, N., and Unmack, A., 1929, Elektrometrische Messungen mit Wasserstoffelektroden in Mischungen von Säuren und Basen mit Salzen: Det Dg. Danske Videnskabernes Selskab. Mat-hematisk-fysiske Meddelelser, v. 9, p. 1–208.

Blandamer, M. J., Burgess, J., and Duce, P. P., 1981, Analysis of the dependence on temperature of the acid dissociation constants for mono-carboxylic acids in water in terms of a two-stage mechanism: Journal of the Chemical Society, Faraday Transactions I, v. 77, p. 2281–2286.

Blumer, M., 1970, Dissolved organic compounds in sea water: saturated and olefinic hydrocarbons and singly branched fatty acids, *in* Hood, D. W., editor, Organic Matter in Natural Waters: University of Alaska, p. 153–167.

Bolton, P. D., Fleming, K. A., and Hall, F. M., 1972, A linear free energy-enthalpy-entropy relationship for the ionization of benzoic acids: Journal of the American Chemical Society, v. 94, p. 1033–1034.

Bonner, O. D., 1982, The osmotic and activity coefficients of lithium, sodium, and potassium trifluoroacetates and a discussion of the ionization of trifluoroacetic acid: Journal of Chemical Thermodynamics, v. 14, p. 275–279.

——— 1988, Osmotic and activity coefficients of the sodium salts of formic, acetic and propionic acids: Journal of Solution Chemistry, v. 17, p. 999–1002.

Bonner, O. D., and Prichard, P. R., 1979, The ionization of trichloroacetic acid and evidence for an unusual type of ion pairing: Journal of Solution Chemistry, v. 8, p. 113–124.

Boon, J. J., Leeuw, J. W., and Burlingame, A. L., 1978, Organic geochemistry of Walvis Bay diatomaceous ooze-III. Structural analysis of the monoenoic and polycyclic fatty acids: Geochimica et Cosmochimica Acta, v. 42, p. 631–644.

Bottei, R. S., and Joern, W. A., 1968, Ionization constants of acetylenedicarboxylic acid: Journal of Chemical and Engineering Data, v. 13, p. 522–523.

Briegleb, G., and Bieber, A., 1951, Dissoziationskonstanten substituierter Benzoesauren bei verschiedened Temperaturen und thermodynamische Groben der Sauredissoziation: Zeitschrift für Elektrochemie, v. 55, p. 250–259.

Briscoe, H. T., and Peake, J. S., 1938, Measurements of the ionization constant of benzoic acid using silver chloride electrodes: Journal of Physical Chemistry, v. 42, p. 637–640.

Britton, H. T. S., 1925, Hydrogen and oxygen electrode titrations of some dibasic acids and of dextrose: Journal of the Chemical Society, v. 127, p. 1896–1917.

Brockman, F. G., and Kilpatrick, M., 1934, The thermodynamic dissociation constant of benzoic acid from conductance measurements: Journal of the American Chemical Society, v. 56, p. 1483–1486.

Bury, C. R., and Davies, D. G., 1932, Specific heats of aqueous solutions of formic, acetic, propionic, and n-butyric acids: Journal of the Chemical Society, v. 1932, p. 2413–2417.

Butler, J. A. V., 1937, The energy and entropy of hydration of organic compounds: Transactions of the Faraday Society, v. 33, p. 229–238.

Butler, J. A. V., and Ramchandani, C. N., 1935, The solubility of non-electrolytes. Part II. The influence of the polar group on the free energy of hydration of aliphatic compounds: Journal of the Chemical Society, v. 1935, p. 952–955.

Cabani, S., and Gianni, P., 1979, Thermodynamic functions of hydration of saturated uncharged organic compounds. Free energies, enthalpies and entropies at 25°C: Journal of the Chemical Society, Faraday Transactions I, v. 75, p. 1184–1195.

Cabani, S., Conti, G., and Matteoli, E., 1978, Heat capacities of hydration of saturated uncharged organic compounds at 25°C: Journal of the Chemical Society, Faraday Transactions I, v. 74, p. 2408–2417.

Cabani, S., Gianni, P., Mollica, V., and Lepori, L., 1981, Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solutions: Journal of Solution Chemistry, v. 10, p. 563–595.

Calis-Van Ginkel, C. H. D., Calis, G. H. M., Timmermans, C. W. M., de Kruif, C. G., and Oonk, H. A. J., 1978, Enthalpies of sublimation and dimerization in the vapour phase of formic, acetic, propanoic, and butanoic acids: Journal of Chemical Thermodynamics, v. 10, p. 1083–1088.

Campbell, A. N., and Campbell, A. J. R., 1934, The thermodynamics of binary liquid mixtures: formic acid and water: Transactions of the Faraday Society, v. 30, p. 1109–1114.

Canady, W. J., Papée, H. M., and Laidler, K. J., 1958, Microcalometric studies of heats of neutralization and ionization of some weak acids in highly dilute aqueous solutions: Transactions of the Faraday Society, v. 54, p. 502–506.

Cannan, R. K., and Kibrick, A., 1938, Complex formation between carboxylic acids and divalent metal cations: Journal of the American Chemical Society, v. 60, p. 2314–2320.

Cappenberg, T. E., Hordijk, K. A., Jonkheer, G. J., and Lauwen, P. M., 1982, Carbon flow across the sediment-water interface in Lake Vechten, The Netherlands: Hydrobiologia, v. 91, p. 161–168.

Cardoso, J. N., and Eglinton, G., 1983, The use of hydroxyacids as geochemical indicators: Geochimica et Cosmochimica Acta, v. 47, p. 723–730.

Carmona, P., and Garcia-Ramos, J. V., 1985, Polarizable proton-transfer hydrogen bonds between phosphate and organic acids: Journal of the Chemical Society, Faraday Transactions 2, v. 81, p. 929–935.

Carothers, W. W., and Kharaka, Y. K., 1978, Aliphatic acid anions in oil-field waters-implications for origin of natural gas: American Association of Petroleum Geologists Bulletin, v. 62, p. 2441–2453.

Chameides, W. L., and Davis, D. D., 1983, Aqueous-phase source of formic acid in clouds: Nature, v. 304, p. 427–429.

Chawla, B., and Ahluwalia, J. C., 1975, Enthalpies and heat capacities of dissolution of some sodium carboxylates in water and hydrophobic hydration: Journal of Solution Chemistry, v. 4, p. 383–389.

Chian, E. S., and DeWalle, F. B., 1977, Characterization of soluble organic matter in leachate: Environmental Science and Technology, v. 11-2, p. 159–163.

Choudhury, N. R., and Ahluwalia, J. C., 1982a, Enthalpies and heat capacities of transfer of sodium carboxylates and sodium dodecylsulfate from water to aqueous tert-Butyl alcohol solutions: Journal of Solution Chemistry, v. 11, p. 189–201.

——— 1982b, Temperature dependence of heat capacities of sodium decanoate, sodium dodecanoate, and sodium dodecyl sulphate, in water: Journal of Chemical Thermodynamics, v. 14, p. 281–289.

Christensen, J. J., Hansen, L. D., and Izatt, R. M., 1976, Handbook of Proton Ionization Heats and Related Thermodynamic Quantities: New York, John Wiley and Sons, 269 p.

Christensen, J. J., Izatt, R. M., and Hansen, L. D., 1967, Thermodynamics of proton ionization in dilute aqueous solution. VII. ΔH° and ΔS° values for proton ionization from carboxylic acids at 25°: Journal of the American Chemical Society, v. 89, p. 213–222.

Christensen, J. J., Oscarson, J. L., and Izatt, R. M., 1968, Thermodynamics of proton ionization in dilute aqueous solution. X. ΔG° (pK), ΔH°, and ΔS° values for proton ionization from several monosubstituted carboxylic acids at 10, 25, and 40°: Journal of the American Chemical Society, v. 90, p. 5949–5953.

Christensen, J. J., Slade, M. D., Smith, D. E., Izatt, R. M., and Tsang, J., 1970, Thermodynamics of proton ionization in dilute aqueous solution. XIII. ΔG° (pK), ΔH°, and ΔS° values for proton ionization from several methyl- and ethyl-substituted aliphatic carboxylic acids at 10, 25, and 40°: Journal of the American Chemical Society, v. 92, p. 4164–4167.

Chueh, C. F., 1974, Predicting activity coefficients of multicomponent solutions containing formic acid, acetic acid, formaldehyde, acetaldehyde and water: American Institute of Chemical Engineers Journal, v. 70, p. 110–119.

Church, R. F. R., and Weiss, M. J., 1970, Diazirines II. Synthesis and properties of small functionalized diazirine molecules. Some observations on the reaction of a diaziridine with the iodine-iodide ion system: Journal of Organic Chemistry, v. 35, p. 2465–2471.

Clark, R. J. H., and Ellis, A. J., 1960, The effect of pressure on the ionization of some benzoic acids: Journal of the Chemical Society, v. 1960, p. 247–254.

Clayton, W. J., and Vosburgh, W. C., 1937, Equilibria in solutions of cadmium and zinc oxalates: Journal of the American Chemical Society, v. 59, p. 2414–2421.

Cohn, E. J., and Edsall, J. T., 1943, Proteins, Amino Acids and Peptides as Ions and Dipolar Ions: New York, Reinhold Publishing Corporation, 686 p.

Connolly, C. A., Walter, L. M., Baadsgaard, H., and Longstaffe, F. J., 1990, Origin and evolution of formation waters, Alberta Bain, Western Canada Sedimentary Basin: Applied Geochemistry, v. 5, p. 375–395.

Cooles, G. P., Mackenzie, A. S., and Parkes, R. J., 1987, Non-hydrocarbons of significance in petroleum exploration: volatile fatty acids and non-hydrocarbon gases: Mineralogical Magazine, v. 51, p. 483–493.

Cooper, J. E., 1962, Fatty acids in recent and ancient sediments and petroleum reservoir waters: Nature, v. 193, p. 744–746.

Cottrell, T. L., Drake, G. W., Levi, D. L., Tully, K. J., and Wolfenden, J. H., 1948, The thermochemistry of solutions. Part V. The heats of ionisation of some organic acids: Journal of the Chemical Society, v. 1948, p. 1016–1019.

Cottrell, T. L., and Wolfenden, J. H., 1948, The thermochemistry of solutions. Part VI. The heat of ionisation of succinic acid: Journal of the Chemical Society, v. 1948, p. 1019–1024.

Cox, J. D., Wagman, D. D., and Medvedev, V. A. (editors), 1989, CODATA key values for thermodynamics: New York, Hemisphere Publishing Corporation, 271 p.

Crawford, M., and Magill, J. H., 1954, The durene effect Part II. The dissociation constants of durene carboxylic and some related acids: Transactions of the Faraday Society, v. 51, p. 704–708.

Crossey, L. J., 1991, Thermal degradation of aqueous oxalate species: Geochimica et Cosmochimica Acta, v. 55, p. 1515–1527.

Crossey, L. J., Frost, B. R., and Surdam, R. C., 1984, Secondary porosity in Laumontite-Bearing Sandstones, *in* McDonald, D. A. and Surdam, R. C., editors, Clastic Diagenesis, chapter 2 Aspects in Porosity Modification: The American Association of Petroleum Geologists Memoir 37, p. 225–237.

Crossey, L. J., Surdam, R. C., and Lahann, R. W., 1986, Application of organic/inorganic diagenesis to porosity prediction, *in* Gautier, D., editor, Roles of organic matter in sediment diagenesis: Society of Economic Paleontologists and Mineralogists Special Publication 38, p. 147–156.

Crutchfield, C. A., Jr., McNabb, W. M., and Hazel, J. F., 1962, Complexes of uranyl ion with some simple organic acids: Journal of Inorganic and Nuclear Chemistry, v. 24, p. 291–298.

Daniel, J., and Cohn, E. J., 1936, Studies in the physical chemistry of amino acids, peptides and related substances. VI. The densities and viscosities of aqueous solutions of amino acids: Journal of the American Chemical Society, v. 58, p. 415–423.

Darken, L. S., 1941, The ionization constants of oxalic acid at 25° from conductance measurements: Journal of the American Chemical Society, v. 63, p. 1007–1011.

Das, S. N., and Ives, D. J. G., 1961, Hydrogen bonding in the acid malonate ion: Proceedings of the Chemical Society of London, v. 1961, p. 373–374.

Davies, C. W., 1935, The reaction of malonic acids with metallic bases: Journal of the Chemical Society, v. 1935, p. 910–912.

———— 1938, The extent of dissociation of salts in water. Part IV. Some calcium salts of organic acids: Journal of the Chemical Society, v. 1938, p. 277–281.

Davies, P. B., and Monk, C. B., 1954, E.M.F. studies of electrolytic dissociation. Part 5. Some glycollates in water: Transactions of the Faraday Society, v. 50, p. 128–132.

Dawson, G. A., and Farmer, J. C., 1988, Soluble atmospheric trace gases in the Southwestern U.S. 2 Organic species HCHO, HCOOH, CH_3COOH: Journal of Geophysical Research, v. 93(5), p. 5200–5206.

De Kruif, C. G., and Oonk, H. A. J., 1979, Enthalpies of vaporization and vapour pressures of seven aliphatic carboxylic acids: Journal of Chemical Thermodynamics, v. 11, p. 287–290.

De Kruif, C. G., and Blok, J. G., 1982, The vapour pressure of benzoic acid: Journal of Chemical Thermodynamics, v. 14, p. 201–206.

De Lisi, R., Perron, G., and Desnoyers, J. E., 1980, Volumetric and thermochemical properties of ionic surfactants: sodium decanoate and octylamine hydrobromide in water: Canadian Journal of Chemistry, v. 58, p. 959–969.

De Lisi, R., Perron, G., Paguette, J., and Desnoyers, J. E., 1981, Thermodynamics of micellar systems: activity and entropy of sodium decanoate and n-alkylamine hydrobromides in water: Canadian Journal of Chemistry, v. 59, p. 1865–1871.

De Robertis, A., De Stefano, C., Rigano, C., and Sammartano, S., 1990, Thermodynamic parameters for the protonation of carboxylic acids in aqueous tetraethlammonium iodide solutions: Journal of Solution Chemistry, v. 19, p. 569–587.

De Wit, H. G. M., Bouwstra, J. A., Blok, J. G., and De Kruif, C. G., 1983, Vapor pressures and lattice energies of oxalic acid, mesotartaric acid, phloroglucinol, myoinositol, and their hydrates: Journal of Chemical Physics, v. 78, p. 1470–1475.

Delben, F., and Crescenzi, V., 1978, The ionization of aliphatic dicarboxylic acids in water: Journal of Solution Chemistry, v. 7, p. 597–604.

Desnoyers, J. E., and Ichhaporia, F. M., 1969, Salting-in and salting-out of polar nonelectrolytes: Canadian Journal of Chemistry, v. 47, p. 4639–4643.

Desnoyers, J. E., Page, R., Perron, G., Fortier, J. L., Leduc, P. A., and Platford, R. F., 1973, Thermodynamics and transport properties of sodium benzoate and hydroxy benzoates in water at 25°C: Canadian Journal of Chemistry, v. 51, p. 2129–2137.

Dickey, P. A., Collins, A. G., and Fajardo, I., 1972, Chemical composition of deep formation waters in southwestern Louisiana: American Association of Petroleum Geologists Bulletin, v. 56, p. 1530–1533.

Diebler, H., Secco, F., and Venturini, M., 1984, The influence of intramolecular hydrogen bonding on proton-transfer reactions. A temperature-jump study of acid-base reactions involving substituted salicylic acids: Journal of Physical Chemistry, v. 88, p. 4229–4232.

Dippy, J. F. J., 1938, Chemical constitution and the dissociation constants of monocarboxylic acids Part X. Saturated aliphatic acids: Journal of the Chemical Society, v. 1938, p. 1222–1227.

——— 1939, The dissociation constants of monocarboxylic acids; their measurement and their significance in theoretical organic chemistry: Chemical Reviews, v. 25, p. 151–211.

Dippy, J. F. J., Hughes, S. R. C., and Laxton, J. W., 1954, Chemical constitution and the dissociation constants of monocarboxylic acids. Part XIII. Some alkylbenzoic acids exhibiting steric effects: Journal of the Chemical Society, v. 1954, p. 1470–1476.

Dippy, J. F. J., and Lewis, R. H., 1936, Chemical constitution and the dissociation constants of monocarboxylic acids. Part V. Further substituted benzoic and phenylacetic acids: Journal of the Chemical Society, v. 1936, p. 644–649.

Dippy, J. F. J., and Lewis, R. H., 1937a, Chemical constitution and the dissociation constants of monocarboxylic acids. Part VI, a) The polarity of vinyl and phenyl groups, b) An apparent linear relationship between dissociation constants and dipole moments: Journal of the Chemical Society, v. 1937, p. 1008–1013.

——— 1937b, Studies of the ortho-effect. Part II. The dissociation constants of some o-substituted acids: Journal of the Chemical Society, v. 1937, p. 1426–1429.

Dippy, J. F. J., and Williams, F. R., 1934, Chemical constitution and the dissociation constants of monocarboxylic acids Part II: Journal of the Chemical Society, v. 1934, p. 1888–1892.

Distéche, A., and Distéche, S., 1965, The effect of pressure on pH and dissociation constants from measurements with buffered and unbuffered glass electrode cells: Journal of the Electrochemical Society, v. 112, p. 350–354.

Dobrogowska, C., Hepler, L. G., and Apelblat, A., 1990, The enthalpies of dilution of aqueous organic acids: oxalic acid and citric acid at 298.15 K: Journal of Chemical Thermodynamics, v. 22, p. 167–172.

Domalski, E. S., 1972, Selected values of heats of combustion and heats of formation of organic compounds containing the elements C, H, N, O, P, and S: Journal of Physical and Chemical Reference Data, v. 1, p. 221–277.

Domalski, E. S., Evans, W. H., and Hearing, E. D., 1984, Heat Capacities and Entropies of Organic Compounds in the Condensed Phase: Journal of Physical and Chemical Reference Data: American Chemical Society and American Institute of Physics for the National Bureau of Standards, v. 13, Supplement No. 1, 286 p.

Domalski, E. S., and Hearing, E. D., 1990, Heat capacities and entropies of organic compounds in the condensed phase, Vol II: Journal of Physical and Chemical Reference Data, v. 19, p. 881–1047.

Dondon, M.-L., 1957a, La dissociation des diacides organiques à chaîne linéaire longue: Journal de Chimie Physique, v. 54, p. 290–303.

——— 1957b, La dissociation des diacides organiques à chaîne courte ou ramifiêe: Journal de Chimie Physique, v. 54, p. 304–313.

Dondon, M.-L., et Pâris, M.-T., 1961, Constantes d'ionization de quelques acides organiques en solvant mixte(eau-alcool et ear-dioxane): Journal de Chimie Physique, v. 58, p. 222–227.

Drucker, C., 1920, Weitere Untersuchungen über die Dissoziation ternärer Elektrolyte: Zeitschrift für Physikalische Chemie, v. 96, p. 381–427.

Drummond, S. E., and Palmer, D. A., 1986, Thermal decarboxylation of acetate. Part II. Boundary conditions for the role of acetate in the primary migratin of natural gas and the transportation of metals in hydrothermal systems: Geochimica et Cosmochimica Acta, v. 50, p. 825–833.

Duboux, M., and Tsamados, D., 1924, Dissociation de quelques acides organiques dissous dans des mélanges d'eau et d'alcool éthylique: Helvetica Chimica Acta, v. 7, p. 855–875.

Duce, R. A., Mohnen, V. A., Zimmerman, P. R., Grosjean, D., Cautreels, W., Chatfield, R., Jaenicke, R., Ogren, J. A., Pellizzari, E. D., and Wallace, G. T., 1983, Organic material in the global troposphere: Reviews of Geophysics, v. 21, p. 921–952.

Dudeney, A. W. L., and Irving, R. J., 1975, Spectrophotometric investigations of aqueous solutions at elevated temperatures: Journal of the Chemical Society, Faraday Transactions I, v. 71, p. 1215–1220.

Eberson, L., and Wadsö, I., 1963, Intramolecular hydrogen bonding as a factor in determining the K_1/K_2 ratios of dicarboxylic acids: Acta Chemica Scandinavica, v. 17, p. 1552–1562.

Eden, M., and Bates, R. G., 1959, Resolution of the dissociation constants of d, l-malic acid from 0° to 50°C: Journal of Research of the National Bureau of Standards, v. 62, p. 161–170.

Edman, J. D., and Surdam, R. C., 1986, Organic-inorganic interactions as a mechanism for porosity enhancement in the Upper Cretaceous Ericson sandstone, Green River Basin, Wyoming, *in* Gautier, D., editor, Roles of organic matter in sediment diagenesis: Society of Economic Paleontologists and Mineralogists Special Publication 38, SEPM, p. 85–109.

Edsall, J. T., 1935, Apparent molal heat capacities of amino acids and other organic compounds: Journal of the American Chemical Society, v. 57, p. 1506–1507.

Eglinton, T. I., Curtis, C. D., and Rowland, S. J., 1987, Generation of water-soluble organic acids from kerogen during hydrous pyrolysis: implications for porosity development: Mineralogical Magazine, v. 51, p. 495–503.

Eisen, E. O., and Joffe, J., 1966, Salt effects in liquid-liquid equilibria: Journal of Chemical and Engineering Data, v. 11, p. 480–484.

Ellis, A. J., 1963, The ionization of acetic, pripionic, n-butyric and benzoic acid in water, from conductance measurements up to 225°: Journal of the Chemical Society, v. 1963, p. 2299–2310.

Ellis, A. J., and Anderson, D. W., 1961, The effect of pressure on the first acid dissociation constants of "sulphurous" and phosphoric acids: Journal of the Chemical Society of London, v. 1961, p. 1765–1767.

Ernst, Z. L., Irving, R. J., and Menashi, J., 1964, Calorimetric determination of the heats of the first and second ionization stages of salicyclic acid: Transactions of the Faraday Society, v. 60, p. 56–61.

Esteso, M. A., Fernandez-Merida, L., Hernandez-Luis, F. F., and Gonzalez-Diaz, O. M., 1989a, Activity coefficients in the system NaCl + Na_2 succinate + H_2O at 25°C: Berichte Bunsengesellschaft Physikalishe Chemie, v. 93, p. 213–217.

Esteso, M. A., Fernandez-Merida, L., Gonzalez-Diaz, O. M., and Hernandez-Luis, F. F., 1989c, Ionic interactions in aqueous solutions of organic electrolytes: the system NaCl + NaHSucc + H_2O at 25°C: Berichte Bunsengesellschaft Physikalishe Chemie, v. 93, p. 1114–1118.

Esteso, M. A., Hernandez-Luis, F. F., Fernandez-Merida, L., and Gonzalez-Diaz, O. M., 1989b, Activity coefficients in mixed-electrolyte solutions at 25°C: Na-formate + NaCl system: Journal of Solution Chemistry, v. 18, p. 265–276.

Everett, D. H., Landsman, D. A., and Pinsent, B. R. W., 1952, The thermodynamics of ionization of some fatty acids: Proceedings of the Royal Society (London), v. A215, p. 403–415.

Everett, D. H., and Wynne-Jones, W. F. K., 1939, The thermodynamics of acid-base equilibria: Transactions of the Faraday Society, v. 35, p. 1380–1401.

Fein, J. B., 1991a, Experimental study of aluminum-, calcium-, and magnesium-acetate complexing at 80°C: Geochimica et Cosmochimica Acta, v. 55, p. 955–964.

——— 1991b, Experimental study of aluminum-oxalate complexing at 80°C: Implications for the formation of secondary porosity within sedimentary reservoirs: Geology, v. 19, p. 1037–1040.

Fernandez, L. P., and Hepler, L. G., 1959, Thermodynamics of aqueous benzoic acid and the entropy of aqueous benzoate ion: Journal of Physical Chemistry, v. 63, p. 110–112.

Fischer, A., Mann, B. R., and Vaughan, J., 1961, Influence of pressure on the Hammett reaction constant: dissociation of benzoic acids and phenylacetic acids: Journal of the Chemical Society, v. 1961, p. 1093–1097.

Fischer, M., and Warneck, P., 1991, The dissociation constants of pyruvic acid: determination by spectrophotometric measurements: Berichte Bunsengesellschaft Physikalishe Chemie, v. 95, p. 523–527.

Fisher, J. B., 1987, Distribution and occurrence of aliphatic acid anions in deep subsurface waters: Geochimica et Cosmochimica Acta, v. 51, p. 2459–2468.

Fisher, J. B., and Boles, J. R., 1990, Water-rock interaction in Tertiary sandstones, San Joaquin basin, California, U.S.A.; Diagenetic controls on water composition: Chemical Geology, v. 82, p. 83–101.

Fisher, J. R., and Barnes, H. L., 1972, The ion-product constant of water to 350°: Journal of Physical Chemistry, v. 76, p. 90–99.

Franzosini, P., Plautz, W. A., and Westrum, E. F., Jr., 1983, Thermophysics of metal aldanoates II. Heat capacities and thermodynamic properties of sodium propanoate: Journal of Chemical Thermodynamics, v. 15, p. 600–618.

Fredenhagen, K., and Liebster, H., 1932, Die Teildrucke und Verteilungszahlen der Essigsäure über ihren wässeringen Lösungen bei 25°C: Zeitschrift für Physikaliche Chemie, Abteilung A, v. 162, p. 449–453.

Fukai, M., Matsuo, T., and Suga, H., 1991, Thermodynamic properties of phase transitions in malonic acid and its deuterated analogue: Thermochimica Acta, v. 183, p. 215–243.

Gane, R., and Ingold, C. K., 1931, Electrometric titration curves of dibasic acids Part IV: Journal of the Chemical Society, v. 1931, p. 2153–2169.

Gary, R., Bates, R. G., and Robinson, R. A., 1965, Dissociation constant of acetic acid in deuterium oxide from 5 to 50°. Reference points for a pD scale: Journal of Physical Chemistry, v. 69, p. 2750–2753.

Gelles, E., and Nancollas, G. H., 1956, Electrochemical studies in the rare earth series. Part 2. Rare earth malonates: Transactions of the Faraday Society, v. 52, p. 680–685.

Gelwicks, J. T., Risatti, J. B., and Hayes, J. M., 1989, Carbon isotope effects associated with autotrophic acetogenesis: Organic Geochemistry, v. 14, p. 441–446.

German, W. L., Jeffrey, G. H., and Vogel, A. I., 1937, The dissociation constants of organic acids. Part XIX. Some unsaturated acids: Journal of the Chemical Society, v. 1937, p. 1604–1612.

German, W. L., and Vogel, A. I., 1936, The primary and secondary dissociation constants of malonic, succinic and glutaric acids by potentiometric titration: Journal of the American Chemical Society, v. 58, p. 1546–1549.

Gianni, P., Mollica, V., and Lepori, L., 1982, A simplified additivity scheme for the estimation of the thermodynamic properties of non-electrolytes in water: Zeitschrift für Physikalische Chemie, Neue Folge, v. 131, p. 1–15.

Giles, M. R., and deBoer, R. B., 1989, Secondary porosity: creation of enhanced porosities in the subsurface from the dissolution of carbonate cements as a result of cooling formation waters: Marine and Petroleum Geology, v. 6, p. 261–269.

———— 1990, Origin and significance of redistributional secondary porosity: Marine and Petroleum Geology, v. 7, p. 378–397.

Giles, M. R., and Marshall, J. D., 1986, Constraints on the development of secondary porosity in the subsurface: re-evaluation of processes: Marine and Petroleum Geology, v. 3, p. 243–255.

Gilkerson, W. R., and Mixon, A. L., 1990, The association of aromatic anions in water: Journal of Solution Chemistry, v. 19, p. 491–505.

Giordano, T. H., 1985, A preliminary evaluation of organic ligands and metal-organic complexing in Mississippi Valley-type ore solutions: Economic Geology, v. 80, p. 96–106.

———— 1990, Organic ligands and metal-organic complexing in ore fluids of sedimentary origin: US Geological Survey Circular 1058, p. 31–41.

Glasoe, P. K., and Hutchison, J. R., 1964, Deuterium isotope effect in the ionization of substituted malonic acids in water and in deuterium oxide: Journal of Physical Chemistry, v. 68, p. 1562–1563.

Glasoe, P. K., and Long, F. A., 1960, Use of glass electrodes to measure acidities in deuterium oxide: Journal of Physical Chemistry, v. 64, p. 188–190.

Gomez, D., Font, R., and Soler, A., 1986, Densities and viscosities of aqueous maleic acid solutions between 25 and 90°C: Journal of Chemistry and Engineering Data, v. 31, p. 391–392.

Gouveia, M. A., and de Carvalho, R. G., 1968, Formation constants of lanthanide alpha-hydroxy-n-valeriate complexes: Journal of Inorganic and Nuclear Chemistry, v. 30, p. 2219–2222.

Graedel, T. E., and Weschler, C. J., 1981, Chemistry within aqueous atmospheric aerosols and raindrops: Reviews of Geophysics and Space Physics, v. 19, p. 505–539.

Graedel, T. E., Hawkins, D. T., and Claxton, L. D., 1986, Atmospheric chemical compounds: Sources, occurence, and bioassay: Orlando, Florida, Academic Press, 732 p.

Graham, E. R., 1941, Colloidal organic acids as factors in the weathering of anorthite: Soil Science, v. 52, p.291–295.

Graustein, W. C., Sollins, P., and Cromack, K., Jr., 1977, Calcium oxalate: occurrence in soils and effect on nutrient and geochemical cycles: Science, v. 198, p. 1252–1254.

Grosjean, D., 1989, Organic acids in southern California air: ambient concentrations, mobile source emissions, in situ formation and removal processes: Environmental Science and Technology, v. 23, p. 1506–1514.

Gruner, J. W., 1922, The origin of sedimentary iron formations: The Biwabik Formation of the Mesabi Range: Economic Geology, v. 17, p. 407–460.

Grunwald, E., 1951, A differential potentiometric method of measuring acid and base dissociation constants: Journal of the American Chemical Society, v. 73, p. 4934–4938.

Guerin, M. R., 1991, Environmental tobacco smoke, *in* Hansen, L. D., and Eatough, D. J., editors, Organic chemistry of the atmosphere: Boston, CRC Press, p. 79–119.

Guilleme, J., and Wojtkowiak, B., 1969a, Étude thermodynamique de la dissociation ionique des acides carboxyliques α-acétyléniques., Partie I: Bulletin de la Societe Chimie de France, v. 9, p. 3007–3012.

——— 1969b, Étude thermodynamique de la dissociation ionique des acides carboxyliques α-acétyléniques., Partie II: Bulletin de la Societe Chimie de France, v. 9, p. 3013–3016.

Gullikson, D. M., Caraway, W. H., and Gates, G. L., 1961, Chemical analysis and electrical resistivity of selected California oilfield waters: Washington, DC, US Department of the Interior, Bureau of Mines Report of Investigations 5736, 21 p.

Guthrie, J. P., 1977, Additivity schemes permitting the estimation of partial molar heat capacities of organic compounds in aqueous solution: Canadian Journal of Chemistry, v. 55, p. 3700–3706.

Haas, J., Shock, E. L., and Sassani, D. C., 1995, Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the REE at high pressures and temperatures, (in prep).

Hála, J., and Okác, A., 1962, Polarographische Verfolgung der Komplexe des Urans mit Propionat, Formidsat und Monochloracetat: Collection of Czechoslovak Chemical Communications, v. 27, p. 1697–1701.

Hama, T., and Handa, N., 1980, Molecular weight distribution and characterization of dissolved organic matter from lake waters: Archiv fuer Hydrobiologie, v. 90, p. 106–120.

Hamann, S. D., and Lim, S. C., 1954, The volume change of ionization of weak electrolytes: Australian Journal of Chemistry, v. 7, p. 329–334.

Hamann, S. D., and Strauss, W., 1955, The chemical effects of pressure: Part 3. Ionization constants at pressures up to 1200 atm: Transactions of the Faraday Society, v. 51, p. 1684–1690.

Hamer, W. J., Burton, J. O., and Acree, S. F., 1940, Second ionization constant and related thermodynamic quantities for malonic acid from 0 to 60°C: Journal of Research of the National Bureau of Standards, v. 24, p. 269–292.

Hanor, J. S., and Workman, A. L., 1986, Distribution of dissolved volatile fatty acids in some Louisiana oil-field brines: Applied Geochemistry, v. 1, p. 37–46.

Hansen, R. S., Miller, F. A., and Christian, S. D., 1955, Activity coefficients of components in the systems water-acetic acid, water-propionic acid and water-n-butyric acid at 25°: Journal of Physical Chemistry, v. 59, p. 391–395.

Harned, H. S., and Ehlers, R. W., 1932, The dissociation constant of acetic acid from 0 to 35 degrees centigrade: Journal of the American Chemical Society, v. 54, p. 1350–1357.

——— 1933a, The dissociation constant of acetic acid from 0 to 60° centigrade: Journal of the American Chemical Society, v. 55, p. 652–656.

——— 1933b, The dissociation constant of propionic acid from 0 to 60°: Journal of the American Chemical Society, v. 55, p. 2379–2383.

Harned, H. S., and Embree, N. D., 1934a, The ionization constant of formic acid from 0 to 60°: Journal of the American Chemical Society, v. 56, p. 1042–1044.

——— 1934b, The temperature variation of ionization constants in aqueous solutions: Journal of the American Chemical Society, v. 56, p. 1050–1053.

——— 1935, the ionization constant of acetic acid in methyl alcohol-water mixtures from 0 to 40°C: Journal of the American Chemical Society, v. 57, p. 1669–1670.

Harned, H. S., and Fallon, L. D., 1939, The second ionization constant of oxalic acid from 0 to 50 degrees: Journal of the American Chemical Society, v. 61, p. 3111–3113.

Harned, H. S., and Hickey, F. C., 1937a, The ionization of acetic acid in aqueous sodium chloride solutions from 0 to 40°: Journal of the American Chemical Society, v. 59, p. 1284–1288.

——— 1937b, The hydrolysis of the acetate ion in sodium chloride solutions: Journal of the American Chemical Society, v. 59, p. 1289–1290.

Harned, H. S., and Owen, B. B., 1930, The thermodynamic properties of weak acids and bases in salt solutions, and an exact method of determining their dissociation constants: Journal of the American Chemical Society, v. 52, p. 5079–5091.

Harned, H. S., and Sutherland, R. O., 1934, The ionization constant of n-butyric acid from 0 to 60°: Journal of the American Chemical Society, v. 56, p. 2039–2041.

Harris, A. L., Thompson, P. T., and Wood, R. H., 1980, Freezing points and enthalpies of dilution of aqueous formic, acetic, propionic, and butyric acids. Free energies and enthalpies of solute-solute interactions: Journal of Solution Chemistry, v. 9, p. 305–324.

Harrison, W. J., and Thyne, G. D., 1992, Predictions of diagenetic reactions in the presence of organic acids: Geochimica et Cosmochimica Acta, v. 56, p. 565–586.

Hartman, H., 1938, The first dissociation constant of ethyl- and phenyl-substituted succinic acids: Recueil des Travaux Chimiques des Pays-Bas, v. 57, p. 697–702.

Hedlund, T., and Öhman, L-O., 1988, Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 19. Composition and stability of aluminum complexes with kojic acid and maltol: Acta Chemica Scandinavica, v. 42, p. 702–709.

Heinz, E., 1951, Untersuchungen über Komplexverbindungen des Calciums: Biochemische Zeitschrift, v. 321, p. 314–342.

Helgeson, H. C., 1992, Calculation of the thermodynamic properties and relative stabilities of aqueous acetic and chloroacetic acids, acetate and chloroacetates, and acetyl and chloroacetyl chlorides at high and low temperatures and pressures: Applied Geochemistry, v. 7, p. 291–308.

Helgeson, H. C., and Amend, J. P., 1994, Relative stabilities of biomolecules and the future of high-temperature solution calorimetry: Thermochemica Acta, (in press).

Helgeson, H. C., and Kirkham, D. H., 1976, Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high pressures and temperatures. III. Equation of state for aqueouis species at infinite dilution: American Journal of Science, v. 276, p. 97–240.

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: American Journal of Science, v. 281, p. 1249–1516.

Helgeson, H. C., Knox, A. M., Owens, C. E., and Shock, E. L., 1993, Petroleum, oil-field waters and authigenic mineral assemblages: Are they in metastable equilibrium in hydrocarbon reservoirs? Geochimica et Cosmochimica Acta, v. 57, p. 3295–3339.

Helgeson, H. C., Knox, A., and Shock, E. L., 1991, Petroleum, oil-field brines and authigenic mineral assemblages: Are they in metastable equilibrium in hydrocarbon reservoirs? (abstract) Fifteenth International Meeting on Organic Geochemistry, Manchester, United Kingdom.

Helgeson, H. C., and Shock, E. L., 1988, Role of oxidation/reduction reactions in the hydrothermal transport and deposition of petroleum: (abstract) Geological Society of American Abstracts with Programs, v. 20, p. A95.

Hennet, R., Crerar, D. A., and Schwartz, J., 1988, Organic complexes in hydrothermal systems: Economic Geology, v. 83, p. 742–764.

Hepler, L. G., 1965, Entropy and volume changes on ionization of aqueouis acids: Journal of Physical Chemistry, v. 69, p. 965–967.

Herlihy, L. J., Galloway, J. N., and Mills, A. L., 1987, Bacterial utilization of formic and acetic acid in rainwater: Atmosphere Environment, v. 21, p. 2397–2402.

Hermans, J., Leach, S. J., and Scheraga, H. A., 1963, Thermodynamic data from difference spectra II. Hydrogen bonding in salicylic acid and its implications for proteins: Journal of the American Chemical Society, v. 85, p. 1390–1395.

Hine, J., and Mookerjee, P. K., 1975, The intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions: Journal of Organic Chemistry,v. 40, p. 292–298.

Hinman,N. W., 1990, Chemical factors influencing the rates and sequences of silica phase transitions: effects of organic constituents: Geochimica et Cosmochimica Acta v. 54, p. 1563–1574.

Hobbie, J. E., Crawford, C. C., and Webb, K. L., 1968, Amino acid flux in an estuary: Science, v. 159, p. 1463–1464.

Høiland, H. 1974a, Pressure dependence of the volumes of ionization of carboxylic acids at 25, 35, and 45°C and 1–1200 bar: Journal of the Chemical Society, Faraday Transactions I, v. 70, p. 1180–1185.

——— 1974b, Additivity relations of partial molal volumes in carboxylic acid series: Acta Chemica Scandinavica, v. A28, p. 699–700.

——— 1975, Volumes of ionization of dicarboxylic acids in aqueous solution from density measurements at 25°C: Journal of the Chemical Society, Faraday Transactions I, v. 71, p. 797–802.

——— 1986, Partial molar volumes of biochemical model compounds in aqueous solution, *in* Hinz, H.-J., editor, Thermodynamic data for biochemistry and biotechnology: New York, Springer-Verlag, p. 1–44.

Høiland, H., and Vikingstand, E., 1975, Partial molal volumes and volumes of ionization of hydroxycarboxylic acids in aqueous solution at 25, 30 and 35°C: Journal of the Chemical Society, Faraday Transactions I, v. 71, p. 2007–2016.

——— 1976, Isentropoic apparent molar compressibilities and compressibilities of ionization of carboxylic acids in aqueous solution: Journal of the Chemical Society, Faraday Transactions I, v. 72, p. 1441–1447.

Howell, H., and Fisher, G. S., 1958, The dissociation constants of some of the terpene acids: Journal of the American Chemical Society, v. 80, p. 6316–6319.

Hu, R., Yen, W., Lin, R. and Yu, Q., 1991, Heats of ionization of acetic acid and halogen-acetic acids in water-ethanol and water-dimethyl formamide mixtures: Thermochimica Acta, v. 183, p. 65–71.

Huang, W. H., and Keller, W. D., 1970, Dissolution of rock-forming silicate minerals in organic acids: simulated first-stage weathering of fresh mineral surfaces: American Mineralogist, v. 55, p. 2076–2094.

——— 1971, Dissolution of clay minerals in dilute organic acids at room temperature: American Mineralogist, v. 56, p. 1082–1095.

——— 1972a, Kinetics and mechanisms of dissolution of Fithian illite in two complexing organic acids, *in* Proceedings of the International Clay Conference, Madrid, Spain: Madrid Tipografia Artistica, p. 321–331.

——— 1972b, Organic acids as agents of chemical weathering of silicate minerals: Nature, v. 239, p. 149–151.

——— 1972c, Geochemical mechanics for the dissolution, transport, and deposition of aluminum in the zone of weathering: Clays and Clay Minerals, v. 20, p. 69–74.

Huang, W. H., and Kiang, W. C., 1972, Laboratory dissolution of plagioclase feldspars in water and organic acids at room temperature: American Mineralogist, v. 57, p. 1849–1859.

Hullett, D. A., and Eisenreich, S. J., 1979, Determination of free and bound fatty acids in river water by high performance liquid chromatography: Analytical Chemistry, v. 51, p. 1953–1960.

Hunter, K. A., and Liss, P. S., 1977, The input of organic material to the oceans: Air-sea interactions and the organic chemical composition of the sea surface: Marine Chemistry, v. 5, p. 361–379.

——— 1981, Organic sea surface films, *in* Duursma, E. K., and Dawson, R., editors, Marine Organic Chemistry: Amsterdam, Elsevier, p. 259–298.

Irving, H., and da Silva, J. J. R. F., 1963, The stabilities of complexes of thallium(I) and the alkali metals with uramildiacetic acid: Journal of the Chemical Society, v. 1963, p. 448–4457.

Ives, D. J. G., 1933, The determination of dissociation constants of monobasic acids: Journal of the Chemical Society,v. 1993, p. 731–737.

Ives, D. J. G., Linstead, R. P., and Riley, H. L., 1933, Investigations of the olefinic acids. Part VIII. Dissociation constants: Journal of the Chemical Society, v. 1993, p. 561–568.

Ives, D. J. G., and Prasad, D., 1970a, An improved calomel electrode: Journal of the Chemical Society, v. (B) 1970, p. 1649–1651.

——— 1970b, Free energies and heats of ionisation of some malonic acids: Journal of the Chemical Society, v. (B) 1970, p. 1652–1654.

Jacob, D. J., 1986, The chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate: Journal of Geophysical Research, v. 91, p. 9807–9826.

Jacob, D. J., Wofsy, S. C., 1988, Photochemistry of biogenic emissions over the Amazon forest: Journal of Geophysical Research, v. 93, p. 1477–1486.

——— 1990, Budgets of reactive nitrogen, hydrocarbons, and ozone over the amazon forest during the wet season: Journal of Geophysical Research, v. 95, p. 16,737–16,754.

Jaffe, R., Albrecht, P., and Oudin, J.-L., 1988a, Carboxylic acids as indicators of oil migration—I. Occurence and geochemical significance of C-22 diastereoisomers of the (17βH, 21βH) C_{30} hopanoic acid in geological samples: Advances in Organic Geochemistry, v. 13, p. 483–488.

———— 1988b, Carboxylic acids as indicators of oil migration: II. Case of the Mahakam Delta, Indonesia: Geochimica et Cosmochimica Acta, v. 52, p. 2599–2607.

Jeffery, G. H., and Vogel, A. I., 1935, The dissociation constants of organic acids. Part XI. The thermodynamic primary dissociation constants of some normal dibasic acids: Journal of the Chemical Society, v. 1935, p. 21–30.

———— 1936, The dissociation constants of organic acids. Part XVI. The thermodynamic primary dissociation constants of some alkylmalonic acids: Journal of the Chemical Society, v. 1936, p. 1756–1761.

———— 1939, The dissociation constants of organic acids. Part XX. The thermodynamic primary dissociation constants of some alkylglutaric acids: Journal of the Chemical Society, v. 1939, p. 447–452.

Jeffries, H. P., 1972, Fatty-acid ecology of a tidal marsh: Limnology and Oceanography, v. 17, p. 433–440.

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 bars and 0° to 1000°C: Computers and Geoscience, v. 18, p. 899–947.

Jones, A. V., and Parton, H. N., 1952, The thermodynamic dissociation constant of benzoic acid and the entropy of the benzoate ion: Transactions of the Faraday Society, v. 48, p. 8–11.

Jones, I., and Soper, F. G., 1936, The effect of temperature on the ionization constants of some dibasic acids: Journal of the Chemical Society, v. 1936, p. 133–137.

Kawaizumi, F., Noguchi, T., andMiyahara, Y., 1977, Heat capacities of aqueous solutions of glutaric and malonic acids: Bulletin of the Chermical Society of Japan, v. 50, p. 1687–1689.

Kawamura, K., and Ishiwatari, R. 1985, Behavior of lipid compounds on laboratory heating of a recent sediment: Geochemical Journal, v. 19, p. 113–126.

Kawamura, K., and Kaplan, I. R., 1984, Capillary gas chromatography determination of volatile organic acids in rain and fog samples: Analytical Chemistry, v. 56, p. 1616–1620.

———— 1990, Stabilities of carboxylic acids and phenols in Los Angeles rainwaters during storage: Water Research, v. 24, p. 1419–1423.

———— 1991, Organic compounds in rainwater, *in* Hansen, L. D., and Eatough, D. J., editors, Organic Chemistry of the Atmosphere: Boston, CRC Press, p. 233–284.

Kawamura, K., Nissenbaum, A., and Gagosian, R. B., 1992, High abundance of low molecular weight organic acids in hypersaline spring water associated with a salt diapir: Organic Geochemistry, v. 18, p. 469–476.

Kawamura, K. Steinberg, S., and Kaplan, I. R., 1985, Capillary GC determination of short-chain dicarboxylic acids in rain, fog, and mist: International Journal of Environmental Analytical Chemistry, v. 19, p. 175–188.

Kawamura, K., Tannenbaum, E., Huizinga, B. J., and Kaplan, I. R., 1986, Volatile organic acids generated from kerogen during laboratory heating: Geochemical Journal, v. 20, p. 51–59.

Kaye, W. A., and Parks, G. S., 1934, The partial pressures of formic and acetic acids above some aqueous solutions; and their partial molal free energies at 1.0 molal concentration: Journal of Chemical Physics, v. 2, p. 141–142.

Keene, W. C., and Galloway, J. N., 1984, Organic acidity in precipitation of North America: Atmospheric Environment, v. 18, p. 2491–2497.

———— 1986, Considerations regarding sources for formic and acetic acids in the troposphere: Journal of Geophysical Research, v. 91, p. 14466–14474.

Keene, W. C., Galloway, J. N., and Holden, J. N., 1983, Measurement of weak organic acidity in precipitation from remote areas of the world: Journal of Geophysical Research, v. 88, p. 5122–5130.

Keene, W. C., Talbot, R. W., Andreae, M. O., Beecher, K., Berresheim, H., Castro, M., Farmer, J. C., Galloway, J. N., Hoffmann, M. R., Li, S. M., Maben, H. R., Munger, J. W., Norton, R. B., Pszenny, A. A. P., Puxbaum, H., Westberg, H., and Winiwarter, W., 1989, An intercomparison of measurement systems for vapor and particulate phase concentrations of formic and acetic acids: Journal of Geophysical Research, v. 94, p. 6457–6471.

Kettler, R. M., Palmer, D. A., and Wesolowski, D. J., 1991, Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175°C: Journal of Solution Chemistry, v. 20, p. 905–927.

Kettler, R. M., Wesolowski, D. J., and Palmer, D. A., 1992, Dissociation quotients of malonic acid in sodium chloride media to 100°C: Journal of Solution Chemistry, v. 21, p. 883–900.

Kharaka, Y. K., Carothers, W. W., and Rosenbauer, R. J., 1983, Thermal decarboxylation of acetic acid: implications for origin of natural gas: Geochimica et Cosmochimica Acta, v. 47, p. 397–402.

Kharaka, Y. K., Law, L. M., Carothers, W. W., and Goerlitz, D. F., 1986, Role of organic species dissolved in formation waters from sedimentary basins in mineral diagenesis: SEPM Special Publications 38, p. 111–122.

Kharaka, Y. K., Maest, A. S.,Carothers, W. W., Law, L. M., Lamothe, P. J., and Fries, T. L., 1987, Geochemistry of metal-rich brines from central Mississippi Salt Dome basin, U.S.A.: Applied Geochemistry, v. 2, p. 543–561.

Kilpatrick, M., Chase, E. F., and Riesch, L. C., 1934, A comparison of the colorimetric, electrometric and catalytic methods for determining hydrogen-ion concentration: Journal of the American Chemical Society, v. 56, p. 2051–203.

Kilpatrick, M., and Eanes, R. D., 1953, The dissociation constants of acids in salt solutions. III. glycolic acid: Journal of the American Chemical Society, v. 75, p. 587.

Kilpatrick, M., and Morse, J. G., 1953, The dissociation constants of acids in salt solutions. VI. Carbocyclic acids: Journal of the American Chemical Society, v. 75, p. 1854–1856.

Kilpi, S., and Meretoja, A., 1937, Die Elektrolytwirkung bei Essigsaure I. Die Dissoziationskonstante in wassrigen Alkali- und Ammoniumchloridlösungen: Zeitschrift für Phsikalische Chemie, v. A179, p. 371–392.

King, E. J., 1957, The thermodynamics of ionization of amino acids. IV. The first ionization constants of some glycine peptides: Journal of the American Chemical Society, v. 79, p. 6151–6156.

——— 1969, Volume changes for ionization of formic, acetic, and n-butyric acids and the glycinium ion in aqueous solution at 25°: Journal of Physical Chemistry, v. 73, p. 1220–1232.

King, E. J., and Prue, J. E., 1961, Precise measurements, with the glass electrode, of the ionization constants of benzoic, phenylacetic, and beta-phenylpropionic acids at 25°: Journal of the Chemical Society, v. 1961, p. 274–279.

Kirkwood, J. G., and Westheimer, F. H., 1938, The electrostatic influence of substituents on the dissociation constants of organic acids: I: Journal of Chemical Physics, v. 6, p. 506–512.

Klingenberg, J. J., Thole, J. P., and Lingg, R. D., 1966, The ionization constants of 13 mandelic acid derivatives were measured in aqueous solution at 25°C using the potentiometric method described by Albert and Serjeant: Journal of Chemical and Engineering Data, v. 11, p. 94–95.

Kolthoff, I. M., and Bosch, W., 1928a, Influence of neutral salts on acid-base equilibria. V. The first and second dissociation constant of succinic acid, tartaric acid and adipinic acid, and the influence of neutral salts on the pH of a mixture of the acid and its acid salt, and the acid salt and normal salt respectively: Recueil des Travaux Chimiques des Pays-Bas, v. 47, p. 861–872.

——— 1928b, Influence of neutral salts on acid-base equilibria. VI. The dissociation constant of acetic acid, capronic acid, benzoic acid and the influence of neutral salts on the dissociation constant of weak acids: Recueil des Travaux Chimiques des Pays-Bas, v. 47, p. 873–882.

——— 1932, The ionization constant of benozoic acid and the activity coefficient of the benzoate ion in presence of neutral salts: Journal of Physical Chemistry, v. 36, p. 1695–1701.

Konicek, J., and Wadsö, I., 1971, Thermochemical properties of some carboxlic acids, amines and n-substituted amides in aqueous solution: Acta Chemica Scandinavica, v. 25, p. 1541–1551.

Koretsky, C. M., and Shock, E. L., 1993, Assessing the role of aqueous metal complexes of monovalent organic ligands in geochemical processes [abstract]: Geological Society of America, Abstracts with Programs, 1993 Annual Meeting, v. 25, p. A-437.

Kortüm, G., and Schöttler, H., 1949, Eine Titrationsmethode zur optischen Bestimmung von Dissoziationskonstanten farbloser Säuren mit Hilfe von Indikatoren: Angewandte Chemie, v. 61, p. 204–208.

Kortüm, G., Vogel, W., and Andrussow, K., 1961, Dissociation constants of organic acids in aqueous solution: London, Butterworths, 536 p.

Kresheck, G. C., and Benjamin, L., 1964, Calorimetric studies of the hydrophobic nature of several protein constituents and ovalbumin in water and in aqueous urea: Journal of Physical Chemistry, v. 68, p. 2476–2486.

Kurz, J. L., and Farrar, J. M., 1969, The entropies of dissociation of some moderately strong acids: Journal of the American Chemical Society, v. 91, p. 6057–6062.

Lamar, W. L., and Goerlitz, D. F., 1966, Organic acids in naturally colored surface waters: United States Geological Survey Water-Supply Paper 1817A.

Land, L. S., and Macpherson, G. L., 1992, Origin of saline formation waters, Cenozoic section, Gulf of Mexico sedimentary basin: American Association of Petroleum Geologists Bulletin, v. 6, p. 1344–1362.

Land, L. S., Macpherson, G. L., and Mack, L. E., 1988, The geochemistry of saline formation waters, Miocene, Offshore Louisiana: Transactions of the Gulf Coast Association of Geological Societies, v. 38, p. 503–511.

Larson, J. W., and Hepler, L. G., 1969, Heats and entropies of ionization, *in* Coetzee, J. F., and Ritchie, C. D., editors, Solute-Solvent Interactions: Marcel Dekker, p. 1–44.

Larsson, E., 1922, Zur elektrolytischen Dissoziation der zweibasischen Säuren. I. Bestimmung der zweiten Dissoziationskonstanten einiger Säuren aus elektrometischen Messungen: Zeitschrift für Anorganische Chemie, v. 125, p. 281–294.

——— 1924, Zur elektrolytischen Dissoziation der zweibasischen Säuren. II. Die zweiten Dissoziationskonstanten einiger Säuren: Zeitschrift für Anorganische Chemistry, v. 140, p. 292–302.

——— 1926, Zur elektrolytischen Dissoziation der zweibasischen Süuren. III. Bestimmung zweiter Dissoziationskonstanten aus Löslichkeitsversuchen: Zeitschrioft für Anorganische Chemie, v. 155, p. 247–254.

——— 1929, Zur elektrolytischen Dissoziation der zweiobasischen Säuren. V. Die Dissoziationskonstanten der drei Monooxybenoesäuren: Zeitschrift für Anorganische Chemie, v. 183, p. 30–36.

——— 1932, Die elektrolytiosche Dissoziation von Säuren in Salzlosungen. IV. Die Dissoziationskonstaten einiger Fettsäuren mit verzweigten Kohlenstoffketten und die Aktivitätsverhältnisse ihrer Ionen in Natriunchlorid-und Kaliumchloridlösungen: Zeitschrift für Physikalische Chemie, v. A159, p. 306–314.

Larsson, E., and Adell, B., 1931a, Die elektrolytische Dissoziation von Sauren in Salzlösungen I. Die Dissoziationskonstanten der Essigsaure und die Aktivitätsverhähnisse ihrer Ionen in den Lösungen einiger Alkali- und Erdalkalichloride: Zeitschrift für Physikalische Chemie, v. 156, p. 352–396.

——— 1931b, Die elektrolytische Dissoziation von Säuren in Salzlosungen II. Die Dissoziaitonskonstanten einiger Fettsäuren und die Aktivitätsverhältnisse ihrer Ionen in Natriumchlorid- und Kaliumchloridlösungen: Zeitschrift für Physikalische Chemie, v. A157, p. 381–396.

——— 1931c, Die elecktrolytische Dissoziation von Säuren in Salzlösungen III. Die Dissoziationskonstanten einiger Säuren und die Aktivitätsverhältnisse iöhrer Ionen in Natriumchlorid-und Kaliumchloridlösungen: Zeitschrift für Physikalische Chemie, v. A157, p. 342–362.

Lawless, J. G., and Yuen, G. U., 1979, Quantification of monocarboxylic acids in the Murchison carbonaceous meteroite: Nature, v. 282, p. 396–398.

Lawless, J. G., Zeitman, B., Pereira, W. E., Summons, R. E., and Duffield, A. M., 1974, Dicarboxylic acids in the Murchison meteorite: Nature, v. 251, p. 40–42.

Leduc, P.-A., and Desnoyers, J. E., 1973, Apparent molal heat capacities and volumes of tetrabutylammonium carboxylates and related solutes in water at 25°C: Canadian Journal of Chemistry, v. 51, p., 2993–2998.

Leung, C. S., and Grunwald, E., 1970, Temperature dependence of $\Delta\overline{C}_p^\circ$ for the self-ionization of water and for the acid dissociation of acetic acid and benzoic acid in water: Journal of Physical Chemistry, v. 74, p. 687–696.

Levien, B. J., 1955, A. physicochemical study of aqueous citric acid solutions: Journal of Physical Chemistry, v. 59, p. 640–644.

Lewis, R. W., 1969, The fatty acid composition of arctic marine phytoplankton and zooplankton with special reference to minor acids: Limnology and Oceanography, v. 14, p. 35–40.

Likens, G. E., Edgerton, E. S., and Galloway, J. N., 1983, The composition and deposition of organic carbon in precipitation: Tellus, Series B, v. 35, p. 16–24.

Lind, C. J., and Hem, J. D., 1975, Effects of Organic Solutes on Chemical Reactions of Aluminum: U.S. Geological Survey Water-Supply Paper 1827-G.

Lindenbaum, S., 1971, Enthalpies of dilution of aqueous solutions of sodium salts of carboxylic acids: Journal of Chemical Thermodynamics, v. 3, p. 625–629.

Lindsay, W. T., Jr., 1980, Estimation of concentration quotients for ionic equilibria in high temperature water: The model substance approach: Proceedings of the 41st International Water Conference, Engineers' Society of Western Pennsylvania, p. 284–294.

Litchinsky, D., Purdie, N., Tomson, M.B., and White, W. D., 1969, A rigorous solution to the problem of interfering dissociation steps in the titration of polybacic acids: Analytical Chemistry, v. 41, p. 1726-1730.

Lloyd, M., Wycherley, V., and Monk, C. B., 1951, The dissociation constants of the cupric salts of some monocarboxylic acids: Journal of the Chemical Society, v. 1951, p. 1786–1789.

Lo Surdo, A., Shin, C., and Millero, F. J., 1978, The apparent molal volume and adiabatic compressibility of some organic solutes in water at 25°C: Journal of Chemical and Engineering Data, v. 23, p. 197–201.

Lochte, H. L., Burnam, C. W., Meyer, H. W. H., 1949, Organic acids produced by high pressure gas wells: The Petroleum Engineer, p. c34–c39.

Lowe, B. M., and Smith, D. G., 1975a, Dissociation constant of benzoic acid in $H_2O + D_2O$ mixtures: Journal of the Chemical Society, Faraday Transactions I, v. 71, p. 389–397.

———— 1975b, Intramolecular hydrogen bonding and the dissociation constant of salicylic acid in $H_2O + D_2O$ mixtures: Journal of the Chemical Society, Faraday Transactions I, v. 71, p. 1379–1386.

Lown, D. A., Thirsk, H. R., Lord Wynne-Jones, 1968, Effect of pressure on ionization equilibria in water 25°C: Transactions of the Faraday Society, v. 64, p. 2073–2080.

———— 1970, Temperature and pressure dependence of the volume of ionization of acetic acid in water from 25 to 225°C and 1 to 3000 bars: Transactions of the Faraday Society, v. 66, p. 51–73.

Lucas, M., and Le Bail, H., 1976, Volume, heat capacity, and spectroscopic studies of solutions of the salts of adamantanecarboxylic acid and tert-butylcarboxylic acid in H_2O and D_2O: Journal of Physical Chemistry, v. 80, p. 2620–2622.

Lundegard, P. D., ms, 1985, Carbon dioxide and organic acids: origin and role in burial diagenesis (Texas Gulf Coast Tertiary): Dissertation, University of Texas at Austin, 144 p.

Lundegard, P. D., and Kharaka, Y. K., 1990, Geochemistry of organic acids in subsurface waters: Field data, experimental data and models: Chemical Modeling of Aqueous Systems II: American Chemical Society Symposium Series, no. 416, p. 169–189.

Lundegard, P. D., and Land, L. S., 1986, Carbon dioxide and organic acids: their role in porosity enhancement and cementation, paleogene of the Texas Gulf Coast: Role of Organic Matter in Mineral Diagenisis, SEPM Special Publications, v. 38, p. 129–146.

———— 1989, Carbonate equilibria and pH-buffering by organic acids-response to changes in pCO_2: Chemical Geology, v. 74, p. 277–287.

Lundegard, P. D., Land, L. S., and Galloway, W. E., 1984, Problem of secondary porosity: Frio Formation (Oligocene), Texas Gulf Coast: Geology, v. 12, p. 399–402.

Lundegard, P. D., and Senftle, J. T., 1987, Hydrous pyrolysis: a tool for the study of organic acid synthesis: Applied Geochemistry, v. 2, p. 605–612.

MacDougall, F. H., and Blumer, D. R., 1933, The activity of each component in aqueous solutions of sulfuric acid and acetic acid: Journal of the American Chemical Society, v. 55, p. 2236–2240.

MacGowan, D. B., and Surdam, R. C., 1988, Difunctional carboxylic acid anions in oilfield waters: Organic Geochemistry, v 12, p. 245–259.

———— 1990a, Importance of organic-inorganic reactions to modeling water-rock interactions during progressive clastic diagenesis, *in* Melchior, D. C., and Bassett, R. L., editors, Chemical Modeling of Aqueous Systems II: Washington, DC, American Chemical Society, Symposium Series 416, p. 494–507.

———— 1990b, Carboxylic acid anions in formation waters, San Joaquin Basin and Louisiana Gulf Coast, USA: Implications for clastic diagenesis: Applied Geochemistry, v. 5, p. 687–701.

MacInnes, D. A., 1926, The ionization of weak electrolytes: Journal of the American Chemical Society, v. 48, p. 2068–2072.

MacInnes, D. A., and Shedlovsky, T., 1932, The determination of the ionization constant of acetic acid, at 25 degrees, from conductance measurements: Journal of the American Chemical Society, v. 54, p. 1429–1438.

Makhatadze, G. I., Medvedkin, V. N., and Privalov, P. L., 1990, Partial molar volumes of polypeptides and their constituent groups in aqueous solution over a broad temperature range: Biopolymers Chemistry, v. 30, p. 1001–1010.

Makhatadze, G. I., and Privalov, P. L., 1990, Heat capacity of proteins I. Partial molar heat capacity of individual amino acid residues in aqueous solution: hydration effect: Journal of Molecular Biology, v. 213, p. 375–384.

Mandal, P. K., Chatterjee, D. K., Seal, B. K., and Basu, A. S., 1978, Viscosity behavior of benzoic acid and benzoate ion in aqueous solution: Journal of Solution Chemistry, v. 7, p. 57–62.

Manley, E. P., and Evans, L. J., 1986, Dissolution of feldspars by low-molecular-weight aliphatic and aromatic acids: Soil Science, v. 141, p. 106–112.

Manzurola, E., and Apelblat, A., 1985, Apparent molar volumes of citric, tartaric, malic, succinic, maleic, and acetic acids in water at 298.15 K: Journal of Chemical Thermodynamics, v. 17, p. 579–584.

Martell, A. E., and Smith, R. M., 1977, Critical Stability Constants Volume 3: Other Organic Ligands: New York, Plenium Press, 495 p.

——— 1982, Critical stability constants Volume 5: First supplement: New York, Plenium Press, 604 p.

Martens, C. S., 1990, Generation of short chain organic acid anions in hydrothermally altered sediments of the Guaymas Basin, Gulf of California: Applied Geochemistry, v. 5, p. 71–76.

Martin, A. W., and Tartar, H. V., 1937, The ionization constants of lactic acid, 0–50°C, from conductance measurements: Journal of the American Chemical Society, v. 59, p. 2672–2675.

Martin, J. F., and Andon, R. J. L., 1982, Thermodynamic properties of organic oxygen compounds Part LII. Molar heat capacity of ethanoic, propanoic, and butanoic acids: Journal of Chemical Thermodynamics, v. 14, p. 679–688.

Mast, M. A., and Drever, J. I., 1987, The effect of oxalate on the dissolution rates of oligoclase and tremolite: Geochimica et Cosmochimica Acta, v. 51, p. 2559–2568.

Mathieson, J. G., and Conway, B. E., 1975, Volume and adiabatic compressibility of optically active and inactive tartaric acids and tartrates: Journal of Solution Chemistry, v. 4, p. 17–23.

Matsui, T., Ko, H. C., and Hepler, L. G., 1974a, Thermodynamics of ionization of benzoic acid and substituted benzoic acids in relation to the Hammett Equation: Canadian Journal of Chemistry, v. 52, p. 2906–2911.

——— 1974b, Calorimetric heats of ionization of aqueous benzoic acid from 5–100°C and derived thermodynamic quantities: Canadian Journal of Chemistry, v. 52, p. 2912–2918.

Matsumoto, G., 1981, Comparative study on organic constituents in polluted and unpolluted inland aquatic environments-II. Features of fatty acids for polluted and unpolluted waters: Water Research, v. 15, p. 779–787.

Matsumoto, G., Ishiwatari, R., and Hanya, T., 1977, Gas chromatographic mass spectrometric identification of phenols and aromatic acids in river waters: Water Research, v. 11, p. 693–698.

Mattoo, B. N., 1956, Spectrophotometric determination of dissociation constants of p-Hydroxy benzoic acid: Transactions of the Faraday Society, v. 52, p. 1462–1465.

McAuley, A., and Nancollas, G. H., 1961, Thermodynamics of ion association. Part VII. Some transition-metal oxalates: Journal of the Chemical Society, v. 1961, p. 2215–2221.

Means, J. L., and Hubbard, N., 1987, Short-chain aliphatic acid anions in deep subsurface brines: a review of their origin, occurrence, properties, and importance and new data on their distribution and geochemical implications in the Palo Duro Basin, Texas: Organic Geochemistry, v. 11, p. 177–191.

Mesmer, R. E., Patterson, C. S., Busey, R. H., and Holmes, H. F., 1989, Ionization of acetic acid in NaCl(aq) media: A potentiometric study to 573 K and 130 bar: Journal of Physical Chemistry, v. 93, p. 7483–7490.

Meyers, P. A., 1976, Dissolved fatty acids in seawater from a fringing reef and a barrier reef at Grand Cayman: Limnology and Oceanography, v. 21, p. 315–319.

——— 1980, Dissolved fatty acids and organic carbon in seawater from the fringing-barrier reef at Discovery Bay, Jamaica: Bulletin of Marine Science, v. 30, p. 657–666.

Meyers, P. A., and Hites, R. A., 1982, Extractable organic compounds in midwest rain and snow: Atmospheric Environment, v. 9, p. 2169–2175.

Miller, S. L., and Smith-Magowan, D., 1990, The thermodynamics of the Krebs Cycle and related compounds: Journal of Physical and Chemical Reference Data, v. 19, p. 1049–1073.

Millero, F. J., 1971, The molal volumes of electrolytes: Chemical Reviews, v. 71, p. 147–176.

Minnick, L. J., and Kilpatrick, M., 1939, Acid-base equilibria in aqueous and non-aqueous solutions: Journal of Physical Chemistry, v. 43, p. 259–274.

Moldovanyi, E. P., ms, 1990, Evolution of Basinal Brines: Elemental and isotopic evolution of formation waters and diagenetic minerals during burial of carbonate sediments, Upper Jurassic Smackover Formation, Southwest Arkansas, U.S. Gulf Coast: Ph.D. thesis, Washington University, St. Louis, Missouri, 247 p.

Moortgat, G. K., Veyret, B., and Lesclaux, R., 1989a, Absorption spectrum and kinetics of the acetylperoxy radical: Journal of Physical Chemistry, v. 93, p. 2362–2368.

——— 1989b, Kinetics of the reaction of HO_2 with $CH_3C(O)O_2$ in the temperature range 253–368K: Chemical Physics Letters, v. 160, p. 443–447.

Morawetz, H., and Choi, L. S., 1986, Ionization equilibria in dicarboxylic acids undergoing conformational transitions: Journal of Physical Chemistry, v. 90, p. 4119–4121.

Morel, J.-P., Fauve, J., Avédikian, L., and Jullard, J., 1974, Solute-solvent interactions in water-tert-butyl alcohol mixtures. III. $\Delta G°$, $\Delta H°$, and $\Delta S°$ for dissociation of aliphatic carboxylic acids in water-rich media: Journal of Solution Chemistry, v. 5, p. 403–415.

Morrison, T. J., 1944, The salting-out effect: Transactions of the Faraday Society, v. 40, p. 43–49.

Morton, C., 1928, The dilution and neutral-salt errors of buffer mixtures: Journal of the Chemical Society, v. 128, p. 1401–1413.

Mueller, H. F., Larson, T. E., and Ferretti, M., 1960, Chromatographic separation and identification of organic acids: Analytical Chemistry, v. 6, p. 687–690.

Muzaffaruddin, M., Salahuddin, and Malik, W. U., 1963, Spectrophotometric and potentiometric studies on the composition and stability of chromium propionate complex: Journal of the Indian Chemical Society, v. 40, p. 467–471.

Nair, V. S. K., 1965, Studies of metal complexes in solution. Part II. Zinc malonate and phthalate: Journal of the Chemical Society, v. 1965, p. 1450–1455.

Ngeyi, S. P., Malik, I., and Westrum, E. F., Jr., 1990, Thermodynamics of alkali alkanoates VII. Heat capacity and thermodynamic functions of potassium acetate from 4 to 585 K: Journal of Chemical Thermodynamics, v. 22, p. 91–98.

Niazi, M. S. K., Shah, S. S., Ali, J., and Khan, M. Z. I., 1990, Thermodynamic dissociation constants of benzoic and nitrobenzoic acids in mixtures of ethanol and 1-propanol with water at 25°C: Journal of Solution Chemistry, v. 19, p. 623–638.

Nicholas, H. J., 1973, Miscellaneous volatile plant products: Phytochemistry, v. 2, p. 381–399.

Nichols, N., Sköld, R., Spink, C., Suurkuusk, J., and Wadsö, I., 1976b, Additivity relations for the heat capacities of non-electrolytes in aqueous solution: Journal of Chemical Thermodynamics, v. 8, p. 1081–1093.

Nichols, N., Sköld, R., Spink, C., and Wadsö, I., 1976a, Thermochemistry of solutions of biochemical model compounds 6, α, ω-dicarboxylic acids, -diamines, and -diols in aqueous solution: Journal of Chemical Thermodynamics, v. 8, p. 993–999.

Nikolaeva, N. M., and Antipina, V. A., 1972, The dissociation constants of oxalic acid in water at temperatures from 25 to 90°C: Izvestiya Sibirskogo Otdeleniya Akademii Nauk SSSR, Ser. Khimiko Nauk, v. 6, p. 13–17.

Nims, L. F., 1936, The ionization constants of glycolic acid from 0 to 50°C: Journal of the American Chemical Society, v. 58, p. 987–989.

Nims, L. F., and Smith, P. K., 1936, The ionization of lactic acid from zero to fifty degrees: Journal of Biological Chemistry, v. 113, p. 145–152.

Norton, R. B., 1985, Measurements of formate and acetate in precipitation at Niwot Ridge and Boulder, Colorado: Geophysical Research Letters, v. 12, p. 769–772.

Norton, R. B., Roberts, J. M., and Huebert, B. J., 1983, Tropospheric oxalate: Geophysical Research Letters, v. 10, p. 517–520.

Noulty, R. A., and Leaist, D. G., 1987, Diffusion coefficient of aqueous benzoic acid at 25°C: Journal of Chemical and Engineering Data, v. 32, p. 418–420.

Novikov, S. S., Ivanov, I. S., Bogdanova, G. V., Alekseeva, T. A., and Konnova, Yu. V., 1966, Synthesis and some chemical transformations of nitro- and nitraza-dicarboxylic acids: Bulletin of the Academy of Sciences of the USSR Division of Chemical Science, Engineering Transactions, p. 719–721.

Noyes, A. A., Kato, Y., and Sosman, R. B., 1910, The hydrolysis of ammonium acetate and the ionization of water at high temperatures: Journal of the American Chemical Society, v. 32, p. 159–178.

Nyrén, V., and Back, E., 1958, The ionization constant, solubility product and solubility of lauric and myristic acid: Acta Chemica Scandinavica, v. 12, p. 1305–1311.

Öjelund, G., and Wadsö, I., 1967, Thermochemistry of ionization reactions for glyoxylic acid, pyruvic acid, and α-ketobutyric acid: Acta Chemica Scandinavica, v. 21, p. 1408–1414.

Ölander, A., 1929, Studien uber Brombernsteinsäure I. Einleitende Untersuchungen: Zeitschrift für Physikalische Chemie, v. 144, p. 49–72.

Oldham, C., 1987, Carboxylates, squarates and related species, *in* Wilkinson, G., editor, Comprehensive Coordination Chemistry. 2. Ligands: Oxford, Pergamon, p. 435–459.

Olofsson, G., 1984, Temperature dependence of the heat-capacity change for the dissociation of acetic acid and of propionic acid in water: Journal of Chemical Thermodynamics, v. 16, p. 39–44.

Ong, H. L., Swanson, V. E., and Bisque, R. E., 1970, Natural organic acids as agents of chemical weathering: United States Geological Survey Professional Paper 700-C, p. C130–C137.

Ong, K. C., Douglas, B., and Robinson, R. A., 1966, Dissociation constants of pyridinepentacarboxylic acid and other pyridinecarboxylic acids: Journal of Chemical and Engineering Data, v. 11, p. 574–577.

Oscarson, J. L., Gillespie, S. E., Christensen, J. J., Izatt, R. M., and Brown, P. R., 1988, Thermodynamic quantities for the interaction of H^+ and Na^+ with $C_2H_3O_2^-$ and Cl^- in aqueous solution from 275 to 320°C: Journal of Solution Chemistry, v. 17, p. 865–885.

Ostiguy, C., Ahluwalia, J. C., Perron, G., and Desnoyers, J. E., 1977, Heat capacities, volumes, and expansibilities of sodium phenyl carboxylates in water: Canadian Journal of Chemistry, v. 55, p. 3368–3370.

Ostwald, W., 1889, Über die Affinitätsgrössen organischer Säuren und ihre Beziehungen zur Zusammensetzung und Konstitution derselben: Zeitschrift für Physikalische Chemie, v. 3, p. 241–288.

Owen, B. B., and Brinkley, S. R., Jr., 1941, Calculation of the effect of pressure upon ionic equilibria in pure water and in salt solutions: Chemical Reviews, v. 29, p. 461–474.

Paabo, M., Bates, R. G., and Robinson, R. A., 1966, Dissociation of acetic acid-d_3 in aqueous solution and related isotope effects from 0 to 50°: Journal of Physical Chemistry, v. 70, p. 540–543.

Pal'chevskii, V. V., Zakharyevskii, M. S., Malinina, E. A., 1960, Thermodynamic characteristics of processes of protolytic dissociation of benzoic and p-oxybenzoic acids: Izd-vo Leningrad Univ. Fiz. i Khimiko, v. 3, p. 95–101.

Palma, M., and Morel, J.-P., 1976, Viscosité des solutions aqueuses d'acides carboxyliques aliphatiques et des carboxylates de potassium à 25°C: Journal de Chimie Physique, v. 73, p. 643–649.

Palmer, D. A., and Drummond, S. E., 1986, Thermal decarboxylation of acetate. Part I. The kineticas and mechanism of reaction in aqueous solution: Geochimica et Cosmochimica Acta, v. 50, p. 813–823.

Panagiotopoulos, A. Z., Willson, R. C., and Reid, R. C., 1988, Phase equilibria in ternary systems with carbon dioxide, water, and carboxylic acid at elevated pressures: Journal of Chemical and Engineering Data, v. 33, p. 321–327.

Papadopoulos, N., and Avranas, A., 1990, Dissociation of dalicyclic acid, 2.4-,2.5- and 2,6-dihydroxybenzoic acids in 1-propanol -water mixtures at 25°C: Journal of Solution Chemistry, v. 20, p. 1–7.

Parks, G. S., and Huffman, H. M., 1932, The free energies of some organic compounds: American Chemical Society Monograph Series 60, 251 p.

Parton, H. N., and Gibbons, R. C., 1939, The thermodynamic dissociation constants of oxalic acid: Transactions of the Faraday Society, v. 35, p. 542–545.

Parton, H. N., and Nicholson, A. J. C., 1939,The thermodynamic dissociation constants of oxalic acid in water and methanol-water mixtures: Transactions of the Faraday Society, v. 35, p. 546–550.

Peltzer, E. T., and Bada, J. L., 1978, alpha-Hydroxycarboxylic acids in the Murchison meteorite: Nature, v. 272, p. 443–444.

——— 1981, Low molecular weight α-hydroxy carboxylic and dicarboxylic acids in reducing marine sediments: Geochimica et Cosmochimica Acta, v. 45, p. 1847–1854.

Peltzer, E. T., Bada, J. L., Schlesinger, G., and Miller, S. L., 1984, The chemical conditions on the parent body of the Murchison meteorite: Some conclusions based on amino, hydroxy and dicarboxylic acids: Advances in Space Research, v. 4, p. 69–74.

Perez-Camino, M. C., Sanchez, E., Balon, M., and Maestre, A., 1985, Thermodynamic functions for the transfer of 1-naphthoic acid from water to mixed aqueous solvents at 298 K: Journal of the Chemical Society, Faraday Transactions I, v. 81, p. 1555–1561.

Perron, G., and Desnoyers, J. E., 1979, Volumes and heat capacities of benzene derivatives in water at 25°C: group additivity of the standard partial molal quantities: Fluid Phase Equilibria, v. 2, p. 239–262.

Pinching, G. D., and Bates, R. G., 1948, Second dissociation constant of oxalic acid from 0 to 50°C, and the pH of certain oxalate buffer solutions: Journal of Research of the National Bureau of Standards, v. 40, p. 405–416.

——— 1950a, First dissociation constant of succinic acid from 0° to 50°C and related thermodynamic quantities: Journal of Research of the National Bureau of Standards, v. 45, p. 444–449.

——— 1950b, Second dissociation constant of succinic acid from 0° to 50°C: Journal of Research of the National Bureau of Standards, v. 45, p. 322–328.

Pronk, J. T., Liem, K., Bos, P., and Kuenen, J. G., 1991, Energy transduction by anaerobic ferric iron respiration in Thibacillus ferrooxidans: Applied and Environmental Microbiology, v. 57, p. 2063–2068.

Purdie, N., Tomson, M. B., and Riemann, N., 1972, The thermodynamics of ionization of polycarboxylic acids: Journal of Solution Chemistry, v. 1, p. 465–476.

Puxbaum, H., Rosenberg, C., Gregori, M., Lanzerstorfer, C., Ober, E., and Winiwarter, W., 1988, Atmospheric concentrations of formic acid and acetic acid and related compounds in eastern and northern Austria: Atmospheric Environment, v. 22, p. 2841–2850.

Ralston, A. W., and Hoerr, C. W., 1942, The solubilities of the normal saturated fatty acids: Journal of Organic Chemistry, v. 7, p. 546–555.

Ramsperger, H. C., and Porter, C. W., 1926, The ultraviolet absorption spectrum of formic acid: Journal of the American Chemical Society, v. 48, p. 1267–1273.

——— 1928, The vapor density of formic acid: Journal of the American Chemical Society, v. 50, p. 3036–3038.

Read, A. J., 1981, Ionization constants of benzoic acid from 25 to 250°C and to 2000 bar: Journal of Solution Chemistry, v. 10, p. 437–450.

Redlich, O., and Bigeleisen, J., 1942, Molal Volumes V: Thermodynamic properties of electrolytes at infinite dilution: Chemical Reviews, v. 30, p. 171–179.

Redlich, O, and Nielsen, L. E., 1942, Molal volumes of solutes. VII. Sodium acetate and acetic acid: Journal of the American Chemical Society, v. 64, p. 761–762.

Reyher, R., 1888, Über die innere Reibung wässeriger Lösungen: Zeitschrift für Physikalische Chemie, v. 2, p. 744–757.

Richards, T. W., and Gucker, F. T., Jr., 1925, An improved differential method for the exact determination of specific heats of aqueous solutions; including results for various salts and organic acids: Journal of the American Chemical Society, v. 47, p. 1876–1893.

Richards, T. W., and Mair, B. J., 1929, The heat of neutralization of acetic acid: Journal of the American Chemical Society, v. 51, p. 737–740.

Robin, P. L., and Rouxhet, P. G., 1978, Characterization of kerogens and study of their evolution by infrared spectroscopy: carbonyl and carboxyl groups: Geochimica et Cosmochimica Acta, v. 42, p. 1341–1349.

Robinson, T., 1980, The organic constituents of higher plants: fourth edition: Massachusetts, Cordus Press, 352 p.

Rosenberg, C., Winiwarter, W., Gregori, M., Pech, G., Casensky, V., and Puxbaum, H., 1988, Determination of inorganic and organic volatile acids, NH_3, SO_4^{2-}, NO_3^- and CL^- in ambient air with an annular diffusion denuder system: Fresenius Zeitschrift für Analatische Chemie, v. 331, p. 1–7.

Rosenholm, J. B., Grigg, R. B., and Hepler, L. G., 1986, Thermodynamic properties of aqueous solutions of surfactants: molar heat capacities and volumes: Journal of Chemical Thermodynamics, v. 18, p. 1153–1163.

Rüterjans, H., Schreiner, F., Sage, U., and Ackermann, T., 1969, Apparent molal heat capacities of aqueous solutions of alkali halides and alkylammonium salts: Journal of Physical Chemistry, v. 73, p. 986–994.

Sahay, H., Kumar, S., Upadhyay, S. N., and Upadhya, Y. D., 1981, Solubility of benzoic acid in aqueous polymeric solutions: Journal of Chemical and Engineering Data, v. 26, p. 181–183.

Sakuma, H., Kusama, M., Munakata, S., Obsumi, T., and Sugawara, S., 1983, The distribution of cigarette smoke components between mainstream and sidestream smoke: Beiträge zur Tabakforschung International, v. 12, p. 63–71.

Sakurai, M., 1973, Apparent molal volumes of some organic electrolytes in a dilute aqueous solution at 5, 25, and 45°C: Bulletin of the Chemical Society of Japan, v. 46, p. 1596–1602.

Salomon, M., 1986, Association of carboxylic acids in aqueous solutions from conductivity data: Journal of Solution Chemistry, v. 15, p. 237–241.

Sampoli, M., Marziano, N. C., and Tortato, C., 1989, Dissociation of trifluoromethanesulfonic acid in aqueous solutions by Raman Spectroscopy: Journal of Physical Chemistry, v. 93, p. 7252–7257.

Sansone, F. J., and Martens, C. S., 1981, Determination of volatile fatty acid turnover rates in organic-rich marine sediments: Marine Chemistry, v. 10, p. 233–247.

——— 1982, Volatile fatty acid cycling in organic-rich marine sediments: Geochimica et Cosmochimica Acta, v. 46, p. 1575–1589.

Sartori, G., Costa, G., and Camus, A., 1952, Equilibri omogenei ed eterogenei delle soluzioni di acido d-tartarico e dei suoi sali. Nota 1. Equilibri di dissociazione dell'acido d-tartarico: Annali de Chimica, v. 42, p. 205–213.

Sassani, D. C., and Shock, E. L., 1990, Speciation and solubility of palladium in aqueous magmatic-hydrothermal solutions: Geology, v. 18, p. 925–928.

———— 1992, Estimation of standard partial molal entropies of aqueous irons at 25°C and 1 bar: Geochimica et Cosmochimica Acta v. 56, p. 3895–3908.

———— 1995, Solubility and transport of platinum-group elements in supercritical fluids: Thermodynamic properties of Ru, Rh, Pd, and Pt solids, ions and complexes to 5 kbar and 1000°C: Geochimica et Cosmochimica Acta, in press.

Saville, G., and Gundry, H. A., 1959, The heats of combustion, solution and ionization of lactic acid: Transactions of the Faraday Society, v. 55, p. 2036–2038.

Saxton, B., and Darken, L. S., 1940, The ionization constants of weak acids at 25 degrees from conductance measurements. A method of extrapolating the data: Journal of the American Chemical Society, v. 62, p. 846–852.

Saxton, B., and Meier, H. F., 1934, The ionization constants of benzoic acid and of the three monochlorobenzoic acids, at 25°C, from conductance measurements: Journal of the American Chemical Society, v. 56, p. 1918–1921.

Saxton, B., and Waters, G. W., 1937,The ionization constant of a-crotonic acid at 25°C from conductance measurements: Journal of the American Chemical Society, v. 59, p. 1048–1049.

Schalscha, E. B., Appelt, H., and Schatz, A., 1967, Chelation as a weathering mechanism. I. Effect of complexing agents on the solubilization of iron from minerals and granodiorite: Geochimica et Cosmochimica Ackta, v. 31, p. 587–596.

Schleusener, J. L., Barnes, H. L., Drummond, S. E., and Palmer, D. A., 1988, Activation parameters and low temperature half-lives for the decarboxylation of acetate in sedimentary basin fluids [abstract]: Geological Society of America Abstracts with Programs, v. 20, p. 150.

Schleusener, J. L., Drummond, S. E., Palmer, D. A., and Barnes, H. L., 1987, Effects of common minerals on acetate decarboxylation kinetics [abstract]: Geological Society of America Abstracts with Programs, v. 19, p. 832–833.

Schnitzer, M., Khan, S. U., and Kodama, H., 1976, The dissolution of micas by fulvic acid: Geoderma, v. 15, p. 381–391.

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: Geochimica et Cosmochimica Acta, v. 57, p. 3835–3846.

———— 1995, Thermodynamics of Strecker synthesis in hydrothermal systems: Origins of Life and Evolution of the Biosphere, v. 25, p. 161–173.

Schwarzenbach, G., 1933, Zur Berechnung Intramolekularer Atomabstände aus den Dissoziationskonstanten zweibasischer Säuren. III. Die Acidität substituierter Malonsäuren in Wasser-Alkohol-Mischungen: Helvetica Chimica Acta, v. 16, p. 529–533.

Seewald, J. S., Seyfried, W. E., Jr., and Thornton, E. C., 1990, Organic-rich sediment alteration: an experimental and theoretical study at elevated temperatures and pressures: Applied Geochemistry, v. 5, p. 193–209.

Seifert, W. K., 1972, Carboxylic acids in petroleum and sediments: Fortschrite der Chemie Organischer Naturstoffe, v. 32, p. 1–49.

Semmler, J., and Irish, D. E., 1988, Vibrational spectral studies of solutions at elevated temperatures and pressures. IX. Acetic acid: Journal of Solution Chemistry, v. 17, p. 805–824.

Sengupta, M., Pal, K., Chakravarti, A., and Mahapatra, P., 1978, Dissociation constants of toluic acids in aqueous solution at different temperatures and study of related thermodynamic parameters: Journal of Chemical and Engineering Data, v. 2, p. 103–107.

Serjeant, E. P., and Dempsey, B., 1979, Ionisation constants of organic acids in aqueous solution: New York, Pergamon Press, p. 4–623.

Servant, J., Kouadio, G., Cros, B., and Delmas, R., 1991, Carboxylic monoacids in the air of Mayombe Forest (Congo): Role of the forest as a source or sink: Journal of Atmospheric Chemistry, v. 12, p. 367–380.

Shah, N. M., and Wright, R. T., 1974, The occurrence of glycolic acid in coastal sea water: Marine Biology, v. 24, p. 121–124.

Shaw, D. G., Alperin, M. J., Reeburgh, W. S., and McIntosh, D. J., 1984, Biogeochemistry of acetate in anoxic sediments of Skan Bay, Alaska: Geochimica et Cosmochimica Acta, v. 48, p. 1819–1825.

Shaw, D. G., and McIntosh, D. J., 1990, Acetate in recent anoxic sediments: Direct and indirect measurements of concentration and turnover rates: Estuarine, Coastal and Shelf Science, v. 31, p. 775–788.

Shimoyama, A., Naraoka, H., Yamamoto, H., and Harada, K., 1986, Carboxylic acids in the Yamato-791198 Carbonaceous Chondrites from Antarctica: Chemistry Letters, v. 1986, p. 1561–1564.

Shock, E. L., 1988, Organic acid metastability in sedimentary basins: Geology, v. 16, p. 886–890.

——— 1989, Corrections to "Organic acid metastability in sedimentary basins": Geology, v. 17, p. 572–573.

——— 1990, Geochemical constraints on the origin of orgnaic compounds in hydrothermal systems: Origins of Life and Evolution of the Biosphere, v. 20, p. 331–367.

——— 1992a, Chemical environments of submarine hydrothermal systems: Origins of Life and Evolution of the Biosphere, v. 22, p. 66–107.

——— 1992b, Stability of peptides in high temperature aqueous solutions: Geochimica et Cosmochimica Acta, v. 56, p. 3481–3491.

——— 1993, Hydrothermal dehydration of aqueous organic compounds: Geochimica et Cosmochimica Acta, v. 57, p. 3341–3349.

——— 1994a, Application of thermodynamic calculations to geochemical processes involving organic acids, *in* Pittman, E. D., and Lewan, M. D., editors, The Role of Organic Acids in Geochemical Processes: New York, Springer-Verlag, p. 270–318.

——— 1994b, Erratum to "Sassani, D. C., and Shock, E. L., 1992, Estimation of standard partial molal entropies of aqueous ions at 25°C and 1 bar. Geochimica et Cosmochimica Acta 56, 3895–3908": Geochimica et Cosmochimica Acta, v. 58, p. 2576–2758.

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: Geochimica et Cosmochimica Acta, v. 52, p. 2009–2036.

——— 1990, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of organic species: Geochimica et Cosmochimica Acta, v. 54, p. 915–945.

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: Geochimica et Cosmochimica Acta, v. 53, p. 2157–2183.

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: Geochimica et Cosmochimica Acta, v. 57, p. 4899–4922.

——— 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: Geochimica et Cosmochimica Acta v. 59, p. 1497–1532.

Shock, E. L., and McKinnon, W. B., 1993, Hydrothermal processing of cometary volatiles-Application to Triton. Icarus, v. 106, p. 464–477.

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 an temperatures: Effective electrostatic radii, dissociation constants, and standard partial molal properties to 1000°C and 5 kb: Journal of the Chemical Society, Faraday Transactions, v. 88, p. 803–826.

Shock, E. L., Sassani, D. C., Willis, M. A., and Sverjensky, D. A., 1995, Correlations among standard molal thermodynamic properties of aqueous cations, oxyanions, acid oxyanions and hydroxide complexes: submitted to Geochimica and Cosmochima Acta.

Shock, E. L., and Schulte, M. D., 1990, Summary and implications of reported amino acid concentrations in the Murchison meteorite: Geochimica et Cosmochimica Acta, v. 54, p. 3159–3173.

——— 1993, The influence of minerals on the distribution of hydrocarbons in hydrothermal petroleum [abstract]: EOS, v. 74, p. 669.

Shock, E. L., and Sverjensky, D. A., 1989, Hydrothermal organometallic complexes of base metals (abstract): Geological Society of America Abstracts with Programs, v. 21, p. A8.

Shvets, V. M., 1971, Concentration and distribution of organic substances in ground water: Doklady Akademia Nauk SSSR, v. 201, p. 247–251.

Shvets, V. M., and Seletskiy, Yu.B., 1968, Organic substances in the thermal water of southern Kamchatka: Doklady Akademia Nauk SSSR, v. 182, p. 188–192.

Sihvonen, V., 1930, Über die elektrometrische Bestimmung der beiden Dissoziationskonstanten zweibasischer Säuren: Zeitschrift für Elektrochemie, v. 36, p. 165–171.

Sijpkes, A. H., Van Rossum, P., Raad, J. S., and Somsen, G., 1989, Heat capacities and volumes of some polybasic carboxylic acids in water at 298.15 K: Journal of Chemical Thermodynamics, v. 21, p. 1061–1067.

Simms, H. S., 1928a, The effect of salts on weak electrolytes. I. Dissociation of weak electrolytes in the presence of salts: Journal of Physical Chemistry, v. 32, p. 1121–1141.

———— 1928b, The effect of salts on weak electrolytes. II. Calculation of overlapping constants: Journal of Physical Chemistry, v. 32, p. 1495–1515.

Smith, R. L., and Oremland, R. S., 1983, Anaerobic oxalate degradation: widespread natural occurrence in aquatic sediments: Applied and Environmental Microbiology, v. 46, p. 106–113.

Smith, R. M., and Martell, A. E., 1989, Critical stability constants-Volume 6: Second supplement: New York, Plenium Press, 643 p.

Smith, R. W., Popp, C. J., and Norman, D. I., 1986, The dissociation of oxy-acids at elevated temperatures: Geochimica et Cosmochimica Acta, v. 50, p. 137–142.

Smolyakov, B. S. 1967, :Izvestiya Sibirskogo Otdeleniya Akademii Nauk SSSR, v. 2, p. 8.

Smolyakov, B. S., and Primanchuk, M. P., 1966, Dissociation constants of benzoic acid at temperatures between 25° and 90°: Russian Journal of Physical Chemistry, v. 40, p. 331–333.

Snell, H., and Greyson, J., 1970, Water structure in solutions of the sodium salts of some aliphatic acids: Journal of Physical Chemistry, v. 74, p. 2148–2152.

Speakman, J. C., 1940, The determination of the thermodynamic dissociation constants of dibasic acids: Journal of the Chemical Society, v. 1941, p. 885–859.

Srivastava, S., DeCicco, M. J., Kuo, E., and le Noble, W. J., 1984, Ionization volumes by means of direct dilatometry: Journal of Solution Chemistry, v. 13, p. 663–671.

Stauffer, T. B., and MacIntyre, W. G., 1970, Dissolved fatty acids in the James River Estuary, Virginia, and adjacent ocean waters: Chesapeake Science, v. 11, p. 216–220.

Steinberg, S. M., and Bada, J. L., 1984, Oxalic, glyoxalic and pyruvic acids in eastern Pacific Ocean waters: Journal of Marine Research, v. 42, p. 697–708.

Stern, J. H., Goeders, B. L., Withers, G. L., and Wujs, S. L., 1979, Enthalpies of transfer of NaCl from water to aqueous mono- and dicarboxylic acids at 25°C: Journal of Chemical and Engineering Data, v. 24, p. 314–315.

Stock, D. I., and Davies, C. W., 1949, The colorimetric measurement of pH, and the dissociation constants of the malonates of some bivalent metals: Journal of the Chemical Society, v. 1949, p. 1371–1374.

Stoessel, R. K., and Pittman, E. D., 1990, Secondary porosity revised: the chemistry of feldspar dissolution by carboxylic acids and anions: American Association of Petroleum Geologists Bulletin, v. 74, p. 1795–1805.

Strehlow, H., and Hildebrandt, P., 1990, The dissociation of trifluoroacetic acid: Ber. Bunsenges, Phys. Chem., v. 94, p. 173–179.

Streitwieser, A., Jr., and Klein, H. S., 1963, Isotope effects on acidity of deuterated formic, acetic, pivalic, and benzoic acids: Journal of the American Chemical Society, v. 85, p. 2759–2763.

Strong, L. E., Blubaugh, D. J., and Cavalli, C. R., 1981, Ionization of aqueous dimethylbenzoic acids: conductance and thermodynamics: Journal of Solution Chemistry, v. 10, p. 811–830.

Strong, L. E., Blubaugh, D. J., Kallmyer, J. B., and Taylor, S. P., 1985, Ionization of multiply substituted methylbenzoic acids in water: conductance and thermodynamics: Journal of Physical Chemistry, v. 89, p. 1318–1326.

Strong, L. E., Brummel, C. L., and Lindower, P., 1987,Thermodynamics of the ionization of four difluorobenzoic and pentafluorobenzoic acids in water: Journal of Solution Chemistry, v. 16, p. 105–124.

Strong, L. E., Brummel, C. L., Ryther, R., Radford, J. R., and Pethybridge, A. D., 1988, Dimerization of some substituted benzoic acids in aqueous solution from conductance measurements: Journal of Solution Chemistry, v. 17, p. 1145–1167.

Strong, L. E., Copeland, T. G., Darragh, M., and Van Waes, C., 1980, Ionization of aqueous toluic acids: conductance and thermodynamics: Journal of Solution Chemistry, v. 9, p. 109–128.

Strong, L. E., Kinney, T., and Fischer, P., 1979, Ionization of aqueous benzoic acid: conductance and thermodynamics: Journal of Solution Chemistry, v. 8, p. 239–345.

Strong, L. E., Neff, R. M., and Whitesel, I., 1989, Thermodynamics of dissolving and solvation processes for benzoic acid and the toluic acids in aqueous solution: Journal of Solution Chemistry, v. 18, p. 101–114.

Strong, L. E., Van Waes, C., and Doolittle, K. H., II, 1982, Ionization of five aqueous fluorobenzoic acids: conductance and thermodynamics: Journal of Solution Chemistry, v. 11, p. 237–258.

Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., 1969, The Chemical Thermodynamics of Organic Compounds: New York, John Wiley and Sons, 865 p.

Stumm, W., Furrer, G., Wieland, E., and Zinder, B., 1985,The effects of complex-forming ligands on the dissolution of oxides and aluminosilicates, *in* Drever, J. I., editor, The Chemistry of Weathering: Dordrecht, D. Reidel, p. 55–74.

Su, F., Calvert, J. G., and Shaw, J. H., 1980, A FT IR Spectroscopic study of the ozone-ethene reaction mechanism in O_2-rich mixtures: Journal of Physical Chemistry, v. 84, p. 239–246.

Surdam, R. C., Boese, S. W., and Crossey, L. J., 1984, The chemistry of secondary porosity, *in* McDonald, D. A. and Surdam, R. C., editors, Clastic Diagenesis: American Association of Petroleum Geologists Memoir 37, p. 127–149.

Surdam, R. C., and Crossey, L. J., 1985, Organic-inorganic reactions during progressive burial: Key to porosity and permeability enhancement and preservation: Royal Society of London Philisophical Transactions Series A 315, p. 135–156.

Surdam, R. C., Crossey, L. J., Hagen, E. S., and Heasler, H. P., 1989, Organic-inorganic interactions and sandstone diagenesis: American Association of Petroleum Geologists Bulletin 73, p. 1–23.

Surdam, R. C., and MacGowan, D. B., 1987, Oilfield waters and sandstone diagenesis: Applied Geochemistry, v. 2, p. 613–619.

Sverjensky, D. A., 1986, Genesis of Mississippi Valley-type lead-zinc deposits: Annual Reviews of Earth and Planetary Sciences, v. 14, p. 177–199.

Taft, R. W., 1983, Protonic acidities and basicities in the gas phase and in solution: Substituent and solvent effects, *in* Taft, R. W., editor, Progress in Physical Organic Chemistry: New York, John Wiley and Sons, p. 247–350.

Talbot, R. W., Andrae, M. O., Berresheim, H., Jacob, D. J., and Beecher, K. M., 1990, Sources and sinks of formic, acetic, and pyruvic acids over Central Amazonia: 2. Wet season: Journal of Geophysical Research, v. 95, p. 16799–16811.

Talbot, R. W., Beecher, K. M., Harriss, R. C., and Cofer, W. R., III, 1988, Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site: Journal of Geophysical Research, v. 93, p. 1638–1652.

Tamaki, K., Ohara, Y., and Watanabe, S., 1989, Solution properties of sodium perfluoroalkanoates. Heats of solution, viscosity β coefficients, and surface tensions: Bulletin of the Chemical Society of Japan, v. 62, p. 2497–2501.

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: American Journal of Science, v. 288, p. 19–98.

Telang, S. A., Korchinski, M., and Hodgson, G. W., 1982, Abundances and transport of ions, nitrogen, and carbon in the Mackenzie River, *in* Degens, E. T., editor, SCOPE/UNEP Transport of Carbon and Minerals in Major World Rivers, Part 1, v. 52: Hamburg, Germany, University of Hamburg, p. 333–346.

Teng, T. T., and Lenzi, F., 1975, Methanesulfonic and trichloroacetic acids: densities of aqueous solutions at 20°, 25°, and 35°C: Journal of Chemical and Engineering Data, v. 20, p. 432–435.

Thornton, E. C., and Seyfried, W. E., Jr., 1987, Reactivity of organic-rich sediment in seawater at 350°C, 500 bars: Experimental and theoretical constraints and implications for the Guaymas Basin hydrothermal system: Geochimica et Cosmochimica Acta, v. 51, p. 1997–2010.

Thurman, E. M., 1985, Organic Geochemistry of Natural Waters: Boston, Martinus Nijhoff/Dr. W. Junk Publishers, 497 p.

Topp, N. E., and Davies, C. W., 1940, The extent of dissociation of salts in water. Part IX. Calcium and barium salts of dicarboxylic acids: Journal of the Chemical Society, v. 1490, p. 87–93.

Travers, J. G., McDurdy, K. G., Dolman, D., and Hepler, L. G., 1975, Glass-electrode measurements over a wide range of temperatures: the ionization constants (5–90°C) and thermodynamics of ionization of aqueous benzoic acid: Journal of Solution Chemistry, v. 4, p. 267–274.

Van Vleet, E. S., and Quinn, J. G., 1979, Early diagenesis of fatty acids and isoprenoid alcohols in estuarine and coastal sediments: Geochimica et Cosmochimica Acta, v. 43, p. 289–303.

Vasil'ev, V. P., and Kochergina, L. A., 1967, Effect of ionic strength on heats of ionisation of salicylic acid in aqueous solution at 25°C: Russian Journal of Physical Chemistry, v. 41, p. 1149–1152.

Vasil'ev, V. A., Shevehenko, E. Ya., Fedyainov, N. V., and Golikov, M. V., 1977, Heat capacity of water solutions of acetic acid at 25°C: (in Russian) Iavanovo, Khimikotekhnologicheske fi institut, v. 20, p. 1557–1559.

Vosburgh, W. C., and Beckman, J. F., 1940, The solubility of cadmium and zinc oxalates in salt solutions: Journal of the American Chemical Society, v. 62, p. 1029–1031.

Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churny, K. L., and Nuttall, R. L., 1982, The NBS table of chemical thermodynamic properties: selected values for inorganic and C_1 and C_2 organic substances in SI units: Journal of Physical and Chemical Reference Data, v. 11, Supplement 2, 392 p.

Wangersky, P. J., and Zika, R. G., 1978, The analysis of organic compounds in seawater; National Resources Council of Canada, Report 3, NRCC #16566.

Waring, W., 1952, Some thermodynamic properties of formic acid: Chemical Reviews, v. 51, p. 171–183.

Watson, G. M., and Felsing, W. A., 1941, The apparent and partial molal volumes of the sodium salts of formic, acetic, propionic and n-butyric acids in aqueous solution: Journal of the American Chemical Society, v. 63, p. 410–412.

Weathers, K. C., Likens, G. E., Bormann, F. H., Bicknell, S. H., Bormann, B. T. Eaton, J. S., Galloway, J. N., Keene, W. C., Kimball, K. D., McDowell, W. H., Siccama, T. G., Smiley, D., Tarrant, R. A., and Daube, B. C., Jr., 1988, Cloud water chemistry from ten sites in North America: Environmental Science and Technology, v. 22, p. 1018–1026.

Wenger, P. E., et Kapétanidis, I., 1960, Etude analytique des acides sêbacique et têtrachlorophtalique en vue du dosage du thorium: Recueil des Travaux Chimiques des Pays-Bas, v. 79, p. 567–573.

Westheimer, F. H., and Kirkwood, J. G., 1938, The electrostatic influence of substituents on the dissociation constants of organic acids. II: Journal of Chemical Physics, v. 6, p. 513–517.

White, G. F., and Jones, H. C., 1910, The conductivity and dissociation of organic acids in aqueous solution at different temperatures: American Chemical Journal, v. 44, p. 159–199.

Wieland, E., and Stumm, W., 1992, Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°: Geochimica et Cosmochimica Acta, v. 56, p. 3339–3355.

Wilcox, C. F., and Leung, C., 1968, Transmission of substituent effects. Dominance of field effects: Journal of the American Chemical Society, v. 90, p. 336–341.

Willard, J. W., Sullivan, J. M., and Kim, Y. K., 1982, Solubility of oxalic acid dihydrate in nitric and sulfuric acid solutions at 0, 25, 50°C: Journal of Chemical and Engineering Data, v. 27, p. 442–445.

Willey, L. M., Kharaka, Y. K., Presser, T. S., Rapp, J. B., and Barnes, I., 1975, Short chain aliphatic acid anions in oil-field waters and their contribution to the measured alkalinity: Geochimica et Cosmochimica Acta, v. 39, p. 1707–1711.

Williams, P. J. le B., 1975, Biological and chemical aspects of dissolved organic material in seawater, *in* Riley, J. P., and Skirrow, G., editors, Chemical Oceanography; 2nd Edition: New York, Academic Press, p. 301–363.

Williams, P. M., 1961, Oceanography: organic acids in pacific ocean waters: Nature, v. 189, p. 219–220.

——— 1968, Organic and inorganic constituents of the Amazon river: Nature, v. 218, p. 937–938.

Wilson, J. M., Gore, N. E., Sawbridge, J. E., and Cardenas-Cruz, F., 1967, Acid-base equilibria of substituted benzoic acids. Part I: Journal of the Chemical Society (B), v. 1967, p. 852–859.

Winfrey, M. R., and Zeikus, J. G., 1979, Microbial methanogenesis and acetate metabolism in a meromictic lake: Applied and Environmental Microbiology, v. 37, p. 213–221.

Winiwarter, W., Puxbaum, G., Fuzzi, S., Facchini, M. C., Orsi, G. Beltz, N., Enderle, K., and Jaeschke, W., 1988, Organic acid gas and liquid-phase measurements in Po Valley fall-winter conditions in the presence of fog: Tellus, v. 40B, p. 348–357.

Wirth, H. E., 1948, The partial molal volume of acetic acid in sodium acetate and in sodium chloride solutions: Journal of the American Chemical Society, v. 70, p. 462–465.
Wogelius, R. A., and Walther, J. V., 1991, Olivine dissolution at 25°C: Effects of pH, CO_2, and organic acids: Geochimica et Cosmochimica Acta, v. 55, p. 943–954.
Wolfenden, R., 1976, Free energies of hydration and hydrolysis of gaseous acetamide: Journal of the American Chemical Society, v. 98, p. 1987–1988.
Workman, A. L., and Hanor, J. S., 1985, Evidence for large-scale vertical migration of dissolved fatty acids in Louisiana oil-field brines: Iberia field, south-central Louisiana: Transactions of the Gulf Coast Association of Geological Societies, v. 35, p. 293–300.
Wright, R. T., and Hobbie, J. E., 1966, Use of glucose and acetate by bacteria and algae in aquatic ecosystems: Ecology, v. 47, p. 447–464.
Wright, R. T., and Shah, N. M., 1975, The trophic role of glycolic acid in coastal seawater. I. Heterotrophic metabolism in seawater and bacterial cultures: Marine Biology, v. 33, p. 175–183.
Yuen, G. Blair, N., Des Marais, D. J., and Chang, S., 1984, Carbon isotope composition of low molecular weight hydrocarbons and monocarboxylic acids from Murchison meteorite: Nature, v. 307, p. 252–254.
Yuen, G. U., and Kvenvolden, K. A., 1973, Monocarboxylic acids in Murray and Murchison carbonaceous meteorites: Nature, v. 246, p. 301–302.
Zana, R., 1977, On the volume changes upon protonation of n-alkylcarboxylate ions and n-alkylamines in aqueous solutions. Extension to the interpretation of volumic effects observed in solutions of molecular ions, polyelectrolytes, micellar detergents, and proteins: Journal of Physical Chemistry, v. 81, p. 1817–1822.
Zawidzki, T. W., Papée, H. M., and Laidler, K. J., 1959, Thermodynamics of ionization processes in aqueous solution: Transactions of the Faraday Society, v. 55, p. 1743–1745.
Zinger, A. S., and Kravchik, T. E., 1970, The simpler organic acids in ground water of the lower volga region (genesis and possible use in prospecting for oil): Doklady Akademia Nauk SSSR, v. 202, p. 218–221.
Zsolnay, A., 1977, Inventory of nonvolatile fatty acids and hydrocarbons in the oceans: Marine Chemistry, v. 5, p. 465–475.