Thermochimica Acta, 36 (1980) 173—178

McBRIDE COEFFICIENTS OF SELECT SULPHUR COMPOUNDS

HOWARD A. BENNETT and AXEL MEISEN

Department of Chemical Engineering, The University of British Columbia, Vancouver, B.C. V6T 1W5 (Canada)

(Received 12 July 1979)

ABSTRACT

McBride coefficients were calculated for H_2S_2, S_2O, S_2, S_3, S_4, S_5, S_6, S_7 and S_8 to provide a power series representation for the specific heat (C_p^0), enthalpy (H_T), entropy (S_T^0) and free energy (F_T^0) at temperatures between 300 and up to 5000 K and at atmospheric pressure.

LIST OF SYMBOLS

A, B, C = coefficients in eqn. (8)
A = matrix defined by Zeleznik and Gordon [5]
$a_1 \ldots a_7$ = McBride coefficients
a_8, a_9, a_{10} = Lagrange multipliers
C_p^0 = standard heat capacity at constant pressure
d_i = vector defined by Zeleznik and Gordon [5]
F_T^0 = standard free energy at temperature T
H_T^0 = standard enthalpy at temperature T
n = number of temperature intervals used in eqn. (1)
R = universal gas constant
S_T^0 = standard entropy at temperature T
T = absolute temperature
x_i = vector of coefficients a_1—a_{10}
x_i^T = transpose of vector x_i
$\hat{y}_T$ = C_p^0, $H_T^0 - H_{298}^0$ or S_T^0 calculated from McBride coefficients
y_T = C_p^0, $H_T^0 - H_{298}^0$ or S_T^0 listed in JANAF tables [3]
Z = scaling factor defined by eqn. (6)
σ = standard deviation defined by eqn. (11)

INTRODUCTION

To predict the performance of Claus furnaces and other operations relevant to the sulphur industry, thermochemical data are needed to calculate the composition of air—hydrogen sulphide mixtures at elevated temperatures [1,2]. The data for many compounds, which are present in equilibrium mixtures, are listed in JANAF tables [3] at 100 K intervals and interpolation is therefore frequently required. Data representation in terms of power series avoids this problem and is better suited for computer applications. McBride et al. [4] published coefficients $a_1, a_2, a_3, a_4, a_5, a_6, a_7$ for various compounds to determine the following thermodynamic properties

$$C_p^0/R = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \tag{1}$$

$$H_T^0/RT = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a^6}{T} \tag{2}$$

$$S_T^0/R = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \tag{3}$$

$$F_T^0/RT = a_1(1 - \ln T) - \frac{a_2}{2} T - \frac{a_3}{6} T^2 - \frac{a_4}{12} T^3 - \frac{a_5}{20} T^4 + \frac{a_6}{T} - a_7 \tag{4}$$

The McBride coefficients for H_2S_2, S_2O, S_3, S_4, S_5, S_6, S_7 and S_8 have not been published previously and are the subject of the present paper.

THEORY

Zeleznik and Gordon [5] have shown that, for any compound i, the coefficients in eqns. (1)—(4) may be obtained by solving the matrix equation

$$\mathbf{A}\,\mathbf{x}_i = \mathbf{d}_i \tag{5}$$

where $\mathbf{x}_i^T = [a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_8, a_9, a_{10}]$. Coefficients a_8, a_9 and a_{10} are Lagrange multipliers. Matrix A is a function of temperature only, whereas $\mathbf{d}_i$ also depends on the heat capacity, enthalpy and entropy of compound i. Since A is ill-conditioned, a scaling factor Z was introduced given by

$$Z = \text{diag}[10^{-7}, 10^{-9}, 10^{-12}, 10^{-15}, 10^{-18}, 10^{-3}, 10^{-6}, 10^{-6}, 10^{-5}, 10^{-5}] \tag{6}$$

Equation (5) may therefore be written as

$$\mathbf{x}_i = (Z\mathbf{A})^{-1} Z\,\mathbf{d}_i \tag{7}$$

The inverse matrix $(Z\mathbf{A})^{-1}$ was evaluated by a double precision computer routine; single precision inversion gave erroneous results [6]. Following the suggestions of McBride et al. [4], two sets of coefficients were calculated for each compound, one for the temperature range 300—1000 K and another for the range 1000—5000 K. However, for H_2S_2, the upper temperature limit was restricted to 2000 K because of the lack of high temperature data. Mackle and O'Hare's values [7], which extended up to 1000 K, were used to calculate the McBride coefficients for H_2S_2. The data were extrapolated to 2000 K to obtain an estimate of the thermodynamic properties at elevated temperatures.

Thermodynamic data for S_2O and S_8 are listed in JANAF tables [3] at 100 K intervals and were used for the calculation of coefficients a_1—a_{10}. Similar information is unavailable for the sulphur polymers S_2, S_3, S_4, S_5, S_6, S_7, but it could be obtained from the heat capacities, enthalpies of formation and entropies given by Rau et al. [8]. The data are summarized in Table 1. The heat capacities, enthalpies and entropies, which are needed for defining

TABLE 1

Heat capacities, enthalpies of formation and entropies for various sulphur polymers [8]

Sulphur polymer	Heat capacity (cal mol^{-1} K^{-1}) $C_p^o = A + 10^{-3}\,BT + 10^5\,C\,T^{-2}$			Enthalpy of formation (kcal mol^{-1}) H_{298}^o	Entropy (cal mol^{-1} K^{-1}) S_{298}^o
	A	*B*	*C*		
S_2	8.54	0.28	−0.79	31.20	54.40
S_3	12.854	1.04	−1.554	33.81	64.39
S_4	19.092	0.783	−2.820	34.84	74.22
S_5	25.558	0.253	−3.771	26.14	73.74
S_6	31.580	0.120	−4.400	24.36	84.60
S_7	37.038	0.613	−4.723	27.17	97.41
S_8	42.670	0.860	−5.110	24.32	102.76

the elements of matrix $\mathbf{d}_i$, were obtained from

$$C_p^0 = A + 10^{-3}\,BT + 10^5\,CT^{-2} \tag{8}$$

by using the following equations

$$\begin{aligned} H_T^0 - H_{298}^0 &= \int_{298}^{T} C_p^0\,dT \\ &= A(T-298) + 5\times10^{-4}\,B(T^2-298^2) - 10^5\,C(1/T-1/298) \end{aligned} \tag{9}$$

and

$$\begin{aligned} S_T^0 - S_{298}^0 &= \int_{298}^{T} (C_p^0/T)\,dT \\ &= A\ln\{T/298\} + 10^{-3}\,B(T-298) - 5\times10^4\,(1/T^2-1/298^2) \end{aligned} \tag{10}$$

The absolute temperature is denoted by T.

The accuracy of the present computational method could be assessed for S_2 since the coefficients a_1—a_7 are given by McBride et al. [4] and since the thermodynamic properties are listed in JANAF tables. The assessment was performed in terms of standard deivations defined as

$$\sigma = [\Sigma\,(\hat{y}_T - y_T)^2/(n-1)]^{1/2} \tag{11}$$

where $\hat{y}_T$ denotes C_p^0, $H_T^0 - H_{298}^0$ or S_T^0 calculated from the McBride coefficients at temperature T; y_T represents the corresponding properties listed in JANAF tables. The properties were determined at 100 K intervals and summed for the ranges 300—1000 K and 1000—5000 K. The number of intervals (n) is therefore eight for the lower range and 41 for the upper range.

TABLE 2

McBride coefficients for various sulphur compounds

Compound	Ref.	Temp. range (K)	McBride coefficients		
			a_1	a_2	a_3
H_2S_2	7	300—1000	2.983841	1.827030×10^{-2}	$-3.377943 \times 10^{-}$
		1000—2000	—4.006376	3.825903×10^{-2}	$-4.484299 \times 10^{-}$
S_2O	3	300—1000	2.981449	1.117787×10^{-2}	$-1.345013 \times 10^{-}$
		1000—5000	5.904741	1.235819×10^{-3}	$-5.453139 \times 10^{-}$
S_3	8	300—1000	1.994550	2.214285×10^{-2}	$-4.199058 \times 10^{-}$
		1000—5000	6.192672	8.281507×10^{-4}	$-1.300452 \times 10^{-}$
S_4	8	300—1000	1.419415	4.014523×10^{-2}	$-7.755356 \times 10^{-}$
		1000—5000	9.087337	9.843155×10^{-4}	$-2.587690 \times 10^{-}$
S_5	8	300—1000	1.889776	5.343961×10^{-2}	$-1.040888 \times 10^{-}$
		1000—5000	12.16487	9.189248×10^{-4}	$-3.478061 \times 10^{-}$
S_6	8	300—1000	3.111956	6.210307×10^{-4}	$-1.210310 \times 10^{-}$
		1000—5000	15.07760	9.862620×10^{-4}	$-4.067890 \times 10^{-}$
S_7	8	300—1000	4.977823	6.648612×10^{-2}	$-1.288477 \times 10^{-}$
		1000—5000	17.77322	1.285839×10^{-3}	$-4.266613 \times 10^{-}$
S_8	8	300—1000	8.134380	6.201076×10^{-2}	$-1.145798 \times 10^{-}$
		1000—5000	20.74677	1.422980×10^{-3}	$-6.253405 \times 10^{-}$
S_2	8	300—1000	2.062335	1.084251×10^{-2}	$-2.060508 \times 10^{-}$
	3	300—1000	2.712902	6.210468×10^{-3}	$-9.188907 \times 10^{-}$
	4	300—1000	2.699935	6.274953×10^{-3}	$-9.287078 \times 10^{-}$
	8	1000—5000	4.155184	2.994199×10^{-4}	$-6.805589 \times 10^{-}$
	3	1000—5000	4.192687	3.777821×10^{-4}	$-1.513399 \times 10^{-}$
	4	1000—5000	4.189693	3.846970×10^{-4}	$-1.556663 \times 10^{-}$

RESULTS AND DISCUSSION

The McBride coefficients for H_2S_2, S_2O and the sulphur polymers S_3 to S_8 are summarized in the upper portion of Table 2. The coefficients show a fairly systematic behaviour with respect to temperature range and, in the case of sulphur polymers, molecular weight. To ensure precise evaluation of the thermodynamic data, it was necessary to express the coefficients in terms of seven significant figures.

The lower portion of Table 2 lists the coefficients a_1—a_7 for S_2 computed from the data of Rau et al. [8] and JANAF tables [3]. The coefficients given by McBride et al. [4] are also shown. The differences are fairly small, but a better means of comparison is provided by Table 3 which gives the standard deviations in thermodynamic properties. The deviations are minor and the agreement is particularly good for the specific heat and entropy. It may therefore be concluded that eqns. (1)—(4), together with the coefficients listed in Table 2, provide a good representation for C_p^0, H_T^0, S_T^0 and F_T^0.

a_4	a_5	a_6	a_7
3.191604×10^{-8}	$-1.133443 \times 10^{-11}$	-1.504930×10^{4}	10.12199
2.276628×10^{-8}	$-4.119618 \times 10^{-12}$	-1.352112×10^{4}	45.19797
7.617597×10^{-9}	$-1.632645 \times 10^{-12}$	-8.074227×10^{3}	12.31663
1.065669×10^{-10}	$-7.670578 \times 10^{-15}$	-8.775336×10^{3}	-2.289682
3.693052×10^{-8}	$-1.216380 \times 10^{-11}$	1.573815×10^{4}	16.00090
2.445527×10^{-11}	$-1.693141 \times 10^{-15}$	1.503796×10^{4}	-3.352772
6.849166×10^{-8}	$-2.264341 \times 10^{-11}$	1.588457×10^{4}	20.17998
4.996914×10^{-11}	$-3.547584 \times 10^{-15}$	1.461462×10^{4}	-15.12070
9.198493×10^{-8}	$-3.042697 \times 10^{-11}$	1.096717×10^{4}	14.28267
6.733600×10^{-11}	$-4.793224 \times 10^{-15}$	9.267043×10^{3}	-33.01131
1.068742×10^{-7}	$-3.532800 \times 10^{-11}$	9.444715×10^{3}	10.83229
7.873088×10^{-11}	$-5.602093 \times 10^{-15}$	7.463789×10^{3}	-44.25087
1.135838×10^{-7}	$-3.749137 \times 10^{-11}$	1.016442×10^{4}	5.633759
8.207413×10^{-11}	$-5.806909 \times 10^{-15}$	8.040461×10^{3}	-53.30151
9.744235×10^{-8}	$-3.135071 \times 10^{-11}$	7.830715×10^{3}	-8.797317
1.211831×10^{-10}	$-8.636866 \times 10^{-15}$	5.589266×10^{3}	-67.70522
1.798278×10^{-8}	$-5.884028 \times 10^{-12}$	1.475241×10^{4}	13.16049
6.495227×10^{-9}	$-1.783366 \times 10^{-12}$	1.450320×10^{4}	10.47553
6.539327×10^{-9}	$-1.780228 \times 10^{-12}$	1.450493×10^{4}	10.53422
1.286454×10^{-11}	$-8.945445 \times 10^{-16}$	1.440128×10^{4}	3.497378
2.928021×10^{-11}	$-2.086213 \times 10^{-15}$	1.418747×10^{4}	3.277442
3.036801×10^{-11}	$-2.179585 \times 10^{-15}$	1.418813×10^{4}	3.29303

TABLE 3

Standard deviations in thermodynamic properties of S_2 between JANAF values and data from McBride et al. [4] and Rau et al. [8]

Thermodynamic property	Temperature range (K)	Standard deviation (σ)	
		McBride et al. [4]	Rau et al. [8]
C_p°	300—1000	0.001	0.028
	1000—5000	0.002	0.058
$H_T^\circ - H_{298}^\circ$	300—1000	0.000	0.008
	1000—5000	0.144	0.189
S_T°	300—1000	0.000	0.052
	1000—5000	0.064	0.047

ACKNOWLEDGEMENT

The financial support of the National Science and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1 H.A. Bennett and A. Meisen, Can. J. Chem. Eng., 51 (1973) 720.
2 A. Meissen and H.A. Bennett, Hydrocarbon Process., 53(11) (1974) 171.
3 D.R. Stull and H. Prophet (Eds.), JANAF Thermochemical Tables, 2nd edn., Natl. Bur. Stand., Washington, D.C., 1971.
4 B.J. McBride, S. Heimel, J.G. Ehlers and S. Gordon, Thermodynamic Properties to 6000 K for 210 Substances Involving the First 18 Elements, NASA Sp-3001, Washington, D.C., 1963.
5 F.J. Zeleznik and S. Gordon, NASA Tech. Note D-767 Washington, D.C., 1961.
6 H.A. Bennett, Ph. D. Thesis, Dep. Chem. Eng., Univ. of British Columbia, Vancouver, B.C., Canada, 1979.
7 H. Mackle and P.A.G. O'Hare, Trans. Faraday Soc., 59 (1963) 309.
8 H. Rau, T.R.N. Kutty and J.R.F. Guedes de Carvalho, J. Chem. Thermodyn., 5 (1973) 291.