

Thermochemical Analyses of Sulphur Compounds: Implications for Atmospheric Sulphur Oxidation

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Abstract: A theoretical study of the thermochemical properties of some common sulphur species present in the atmosphere including the intermediates and end-product of their transformation is reported here. These properties were obtained from the approximation of the Schrödinger equation as applied in Gaussian 03 (G03) model chemistry package. Analyses of the chemical reaction equilibrium for a variety of atmospheric sulphur transformations were investigated with a view to establish the thermodynamically favourable reaction pathways over ambient tropospheric temperature range of between -50 and +50°C. Seven high-energy accuracy model chemistries methods integrated in G03 comprising several *ab initio* methods and density functional theory (DFT) methods were applied for the computation. The computational methods were tested with a number of basis sets to yield values approximating those of experimental observations. Of all chosen methods, the complete basis set (CBS-Q) method was observed to closely approximate the experimentally determined thermodynamic enthalpies and Gibbs free energies of reactions. The CBS-Q method produced a mean absolute deviation (MAD) of 1.08% as against experimental data. Of the gas-phase and aqueous-phase reactions about 80 and 59.6%, respectively will most likely attain equilibrium over a temperature range of between -100 and +100°C. Whilst about 15 and 23.4% will not like reach equilibrium the specified temperature range and about 5 and 17% may attain equilibrium at higher temperatures above 20°C. The 4 most important oxidising species involved in the gas-phase reactions of atmospheric SO₂ have been characterized in an order of increasing oxidant's potentials in the form CH₃O₂* < HO₂* < OH* < O*.

Key words: Thermochemistry (analysis), energies, sulphur, atmosphere, reactions

INTRODUCTION

Sulphur compounds emitted from both anthropogenic and biogenic activities into the atmosphere undergo chemical transformation under suitable atmospheric conditions dictated by the meteorology of the troposphere (Ahlberg *et al.*, 1978; Benkovitz *et al.*, 1994; Eliassen and Saltbones, 1983; Tang *et al.*, 1981; Tuncel *et al.*, 1985; Stockwell, 1986; Walcek *et al.*, 1986). These compounds end up generating sub-micron particulate, acidic and neutral sulphate salts in advection plumes away from the source area (Latimer and Samuelson, 1978; Seinfeld and Pandis, 1998; Terblanche *et al.*, 1993). Tropospheric sulphates efficiently scatter light rays of solar radiation and hence contribute to direct forcing of climate. These sulphates can act as cloud condensation nuclei (CCN) and have

been described to display deleterious properties as particulate matter than as deposited acids (Seinfeld and Pandis, 1998; Bari *et al.*, 2003a; 2003b; Newman *et al.*, 1975; Priest *et al.*, 1981; Ross, 2003; Twomey, 1991). High levels of sulphur species which include hydrogen sulphide, sulphur dioxide have been recorded in areas where coal fired power stations, open cast coalmines and crude oil refining plants are located (Bari *et al.*, 2003a; 2003b; Annegarn *et al.*, 1996). Several chemical reactions occur within the mixed layer in the troposphere. These reactions have motivated studies such as smog chamber experiments of numerous chemical reaction mechanisms for the oxidation of trace gaseous and aqueous sulphur species (Carmichael and Peters, 1984; Warneck, 1999; Eggleton and Cox, 1978; Breytenbach *et al.*, 1994; Herrmann *et al.*, 2000).

Fossil fuel processing and combustion processes are generally recognized as the major sources of H_2S and SO_2 in the atmosphere (Terblanche *et al.*, 1993; Bari *et al.*, 2003a, b; Annegarn *et al.*, 1996; Eggleton and Cox, 1978; Warneck, 1988). In previous studies (Warneck, 1999; Breytenbach *et al.*, 1994; Calvert *et al.*, 1978; Grgic and Bercic, 2001; Herrmann *et al.*, 2000; Pienaar and Helas, 1996; Podkrajsek *et al.*, 2004), the reaction pathways taken by the various atmospheric sulphur species during transformation have been determined principally from experimental observations of the gas phase, aqueous phase, radical reactions. The nature and characteristic behaviours of a variety of sulphur species in the atmosphere has been well established, with detailed information on their transformation modes at different atmospheric conditions. Also, available are some thermochemical properties of these species derived from a variety of experimental techniques such as calorimetry, mass spectrometry and pulse radiolysis (Larsen *et al.*, 2001). Despite much research on atmospheric transformation of sulphur-based compounds, a large fraction of the proposed reacting species and reaction mechanisms of sulphur (Warneck, 1999; Calvert *et al.*, 1978; Herrmann *et al.*, 2000; Somnitz *et al.*, 2003), have not been studied with a view to examine their thermodynamic favourability, which is indicative of the potential of these species reacting in the atmosphere. The thermodynamic favourability of the atmospheric reaction types for different reaction temperatures enables the prediction of the most likely products species within a particular location over the ambient temperatures.

A number of atmospheric sulphur transformations are expected over the Mpumalanga Highveld area due to the presence of power generating and hydrocarbon fuel processing plants as well as the vast opencast coalmines within the area (Terblanche *et al.*, 1993; Annegarn *et al.*, 1996). The predominant sulphur species observed in the area are hydrogen sulphide and sulphur dioxide. Hence, this study is aimed at establishing relative importance of the various reactions in order to predict the expected products of transformation over the Mpumalanga Highveld area. In deciding this relative importance by which the atmospheric transformation occurs, some forty-six gas-phase and forty-six aqueous-phase atmospheric sulphur reactions involving H_2S and SO_2 disappearances (Warneck, 1999; Eggleton and Cox, 1978; Calvert *et al.*, 1978; Herrmann *et al.*, 2000; Pienaar and Helas, 1996; Larsen *et al.*, 2001; Somnitz *et al.*, 2003; Barnes *et al.*, 1986; Beilke and Gravenhorst, 1978; Britton and Clarke, 1980; Eisele and Tanner, 1991; Hegg and Hobbs, 1980; Moller, 1980; Viggiano *et al.*, 1980, 1982; Warneck, 1988; Seinfeld and Pandis, 1998), have been considered in this

study (Table 1 and 2). In the literature, there have been only a few theoretical studies of reactions involving sulphur systems using empirical *ab initio* (Alkorta, 1994; Bachrach and Mulhearn, 1996; Çakmak and Srivastava, 1999; Markham and Bock, 1993; Maulitz *et al.*, 1995; Grant and Richards, 1995; Hirst, 1990; Jensen, 1999) and high-level molecular orbital methods (Dunbar and Petrie, 2005; Foresman and Frisch, 1996; Khachatryan *et al.*, 2004; McKee, 1996; Morgan *et al.*, 1997; Parthiban *et al.*, 2003; Yang *et al.*, 1995) but there seems to be no reported thermochemical energy computation for isodesmic reactions involving atmospheric reactions with compounded methods. While, for atmospheric chemistry application only very few applications of molecular orbital theories have been recorded (Parthiban *et al.*, 2003).

The relative importance of a chemical reaction is a measure of the significance of a reaction in relation to the other specified reactions with the same reactant species (Warneck, 1999). The relative importance of a particular reaction over several others aid in the prediction of expected reaction products based on the favourability and rate of reaction. The variability of reaction products with the same starting reactants depends on the thermodynamics of the reaction and the thermochemical properties of the reacting species (Levenspiel, 1999; Satterfield, 1991). In the past, only reaction rate constants, (Warneck, 1999; Calvert *et al.*, 1978; Herrmann *et al.*, 2000; Pienaar and Helas, 1996) have been used to determine the relative importance without any consideration on the thermochemistry to establish the favourability of one reaction against another over the same reaction conditions. Several gas- and aqueous-phase reactions have been proposed for the chemical transformation of atmospheric H_2S and SO_2 in addition to establishing the relative importance of the various reactions with respect to the rate of reaction (Warneck, 1999; Calvert *et al.*, 1978; Pienaar and Helas, 1996). Also, the aqueous phase reactions are known to be more favourable than the gas-phase reactions (Herrmann *et al.*, 2000; Moller, 1980). In this study, the tool of chemical thermodynamics was applied to predict the favourability and feasibility of H_2S and SO_2 transformations, the common reaction path(s) taken by the sulphur gases over a large ambient temperature range of between -50 and $+50^\circ\text{C}$ attainable in the troposphere (Seinfeld and Pandis, 1998). In addition the equilibrium conversion which is governed by the equilibrium constant changes with temperatures was evaluated (Elliott and Carl, 1999; Smith *et al.*, 2004). The analyses were achieved using the electronic model theories of computational chemistry.

In any chemical reaction, the equilibrium relationship between reactants and product is easily modelled using

Table 1: Calculated and experimental enthalpies and Gibbs free energies of the gas-phase reactions

S/no	Gas phase reactions	$\Delta H_{298K} \text{ kJ mol}^{-1}$			$\Delta G_{298K} \text{ kJ mol}^{-1}$		
		B3LYP	CBS-Q	Experiment	B3LYP	CBS-Q	Experiment
1	$\text{H}_2\text{S} + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{SH}^*$	-109.6	-115.4	-117.6*	-108.7	-114.5	NA
2	$\text{HS}^* + \text{O}_2 \rightarrow \text{SO}^* + \text{OH}^*$	-78.5	-100.7	-98.7*	-79.4	-101.6	NA
3	$\text{HS}^* + \text{O}_2 \rightarrow \text{SO}_2 + \text{H}^*$	-130.2	-219.8	-212.8*	-120.0	-135.9	NA
4	$\text{HS}^* + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$	-331.8	-315.4	-289.7*	-336.8	-320.9	NA
5	$\text{HS}^* + \text{O}_3 \rightarrow \text{OH}^* + \text{SO}^* + \text{O}^*$	-16.4	6.1	7.8*	-53.0	-30.8	NA
6	$\text{HSO}^* + \text{O}_2 \rightarrow \text{HO}_2^* + \text{SO}^*$	37.8	48.2	23.6*	36.5	47.2	NA
7	$\text{HSO}^* + \text{O}_2 \rightarrow \text{OH}^* + \text{SO}^* + \text{O}_2$	-127.3	-70.5	-94.4*	-164.8	-107.8	NA
8	$\text{SO}_2 + \text{O}^* \rightarrow \text{SO}_3$	-298.5	-342.9	-348.1*,-348.5*	-260.1	-378.1	-302.8*
9	$\text{SO}_2 + \text{OH}^* \rightarrow \text{HOSO}_2^*$	-92.3	-118.3	-127.5*,-154.8*	-51.4	-151.1	NA
10	$\text{HOSO}_2^* + \text{O}_2 \rightarrow \text{HO}_2^* + \text{SO}_3$	21.0	0.9	3.9*	19.0	-1.2	NA
11	$\text{SO}_2 + \text{HO}_2^* \rightarrow \text{OH}^* + \text{SO}_3$	-20.8	-69.6	-74.1*,-80.8*	-12.8	-135.2	NA
12	$\text{SO}_2 + \text{HO}_2^* \rightarrow \text{HO}_2\text{SO}_2^*$	114.0	3.2	-29.3*	129.2	-22.5	NA
13	$\text{HO}_2\text{SO}_2^* \rightarrow \text{HO}^* + \text{SO}_3$	-134.9	-72.7	-50.2*	-142.0	-112.7	NA
14	$\text{SO}_2 + \text{CH}_3\text{O}^* \rightarrow \text{CH}_3\text{OSO}_2^*$	-498.1	-89.8	-100.4*	-417.8	-111.4	NA
15	$\text{SO}_2 + \text{CH}_3\text{O}_2^* \rightarrow \text{CH}_3\text{O}^* + \text{SO}_3$	-50.4	96.5	-90.7*,-113.0*	-48.1	23.6	NA
16	$\text{SO}_2 + \text{CH}_3\text{CHOO}^* \rightarrow \text{CH}_3\text{CHO}^* + \text{SO}_3$	199.4	174.6	NA	200.5	100.8	NA
17	$\text{SO}_2 + (\text{CH}_3)_2\text{CO}_2^* \rightarrow (\text{CH}_3)_2\text{CO}^* + \text{SO}_3$	-40.7	-69.2	-108.8*	-40.4	-143.3	NA
18	$\text{SO}_2 + \text{CH}_3\text{COO}_2^* \rightarrow \text{CH}_3\text{CO}_2^* + \text{SO}_3$	-98.8	-113.3	-134.4*,-138.1*	-92.5	-188.3	NA
19	$\text{SO}_2 + \text{CH}_3\text{COO}_2^* \rightarrow \text{CH}_3\text{COO}_2\text{SO}_2^*$	19.3	-22.8	-154.8*	73.3	-47.3	NA
20	$\text{SO}_2 + \text{O}_3 \rightarrow \text{O}_2 + \text{SO}_3$	-236.4	-236.1	-241.6*,-241.9*	-233.7	-307.3	-234.2*
21	$\text{SO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{SO}_3$	14.5	-29.5	-41.7*,-41.8*	19.5	-98.3	-39.5*
22	$\text{SO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{SO}_3$	-83.7	-139.4	-138.4*,-137.2*	-81.2	-216.6	NA
23	$\text{SO}_2 + \text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \text{SO}_3$	49.3	-59.9	-101.0*,-102.9*	47.7	-131.9	-88.2*
24	$\text{OCS} + \text{O}^* \rightarrow \text{CO} + \text{SO}$	-196.0	-205.2	-185.5*	-206.6	-215.6	NA
25	$\text{OCS} + \text{OH}^* \rightarrow \text{CO}_2 + \text{HS}$	-148.5	-143.7	-120.7*	-147.3	-142.5	NA
26	$\text{SO}^* + \text{O}^* \rightarrow \text{SO}_2$	-482.1	-548.2	-551.0*	-444.5	-436.7	NA
27	$\text{SO}^* + \text{SO}^* \rightarrow \text{S} + \text{SO}_2$	23.9	-24.9	-29.6*	34.1	59.2	NA
28	$\text{SO}^* + \text{OH}^* \rightarrow \text{H} + \text{SO}_2$	-51.7	-119.1	-123.2*	-40.6	-34.3	NA
29	$\text{SO}^* + \text{SO}_3 \rightarrow \text{SO}_2 + \text{SO}_2$	-183.6	-205.3	-202.9*	-184.4	-58.7	NA
30	$\text{SO}^* + \text{NO}_2 \rightarrow \text{NO} + \text{SO}_2$	-169.1	-234.9	-244.7*	-165.0	-157.0	NA
31	$\text{SO}^* + \text{O}_2 \rightarrow \text{O}^* + \text{SO}_2$	22.7	-49.6	-52.6*	30.4	31.9	NA
32	$\text{SO}^* + \text{O}_2 \rightarrow \text{SO}_3$	-275.8	-392.4	-400.7*	-229.7	-346.2	NA
33	$\text{SO}^* + \text{O}_3 \rightarrow \text{O}^* + \text{SO}_3$	-213.8	-285.7	-294.2*	-203.3	-275.3	NA
34	$\text{SO}^* + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2$	-420.0	-441.5	-444.5*	-418.1	-365.9	NA
35	$\text{HOSO}_2^* + \text{O}_2 \rightarrow \text{HOSO}_2\text{OO}^*$	-1.3	-60.7	-66.9*	46.4	-10.9	NA
36	$\text{HOSO}_2\text{OO}^* + \text{NO} \rightarrow \text{HOSO}_2\text{O}^* + \text{NO}_2$	-1.2	94.9	-104.6*	-8.8	85.9	NA
37	$\text{HOSO}_2\text{OO}^* + \text{NO}_2 \rightarrow \text{HOSO}_2\text{O}^* + \text{NO}_3$	97.0	204.8	-8.4*	91.8	204.2	NA
38	$\text{HOSO}_2\text{OO}^* + \text{HO}_2 \rightarrow \text{HOSO}_2\text{O}_2\text{H} + \text{O}_2$	-179.3	-196.7	-179.9*	-171.1	-190.0	NA
39	$2\text{HOSO}_2\text{OO}^* \rightarrow 2\text{HOSO}_2\text{O}^* + \text{O}_2$	118.8	317.9	-92.0*	66.5	262.7	NA
40	$\text{HOSO}_2\text{O}^* + \text{NO} \rightarrow \text{HOSO}_2\text{ONO}^*$	-246.5	-358.5	-108.8*	-200.1	-309.0	NA
41	$\text{HOSO}_2\text{O}^* + \text{NO}_2 \rightarrow \text{HOSO}_2\text{ONO}_2^*$	-75.2	-194.3	-92.0*	-23.6	-145.9	NA
42	$\text{HOSO}_2\text{O}^* + \text{HO}_2 \rightarrow \text{HOSO}_2\text{OH} + \text{O}_2$	-342.9	-452.6	-238.5*	-334.5	-439.4	NA
43	$\text{HOSO}_2\text{ONO}^* + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{HNO}_2$	-14.7	-9.2	NA	-16.5	-8.9	NA
44	$\text{HOSO}_2\text{ONO}_2^* + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{HNO}_3$	-178.4	-169.2	NA	-178.6	-161.2	NA
45	$\text{SO}_3 + \text{O}^* \rightarrow \text{SO}_2 + \text{O}_2$	-206.3	-155.8	-150.3*,-150.2*	-214.9	-90.6	-160.7*
46	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	-53.2	-84.8	-92.6*,-102.9*	-9.8	-36.0	-53.8*

In all the reactions involving O_2 in air, the O_2 is the dominant reactant. * Enthalpies and free energies for the gas phase reactions were determined from individual enthalpies of formation obtained from Yaws, 1999 and Lide, 2002. All reaction were obtained courtesy of Becker, a Calvert *et al.* (1978), Eggleton and Cox (1978), Hegg and Hobbs (1980), Britton and Clarke (1980), Moller (1980), Warneck (1988), Eisele and Tanner (1991), Pienaar and Helas (1996), Seinfeld and Pandis (1998) and Warneck (1999)

Table 2: Calculated and experimental enthalpies and Gibbs free energies of the aqueous-phase reactions

S/no	Aqueous phase reactions	$\Delta H_{298K} \text{ kJ mol}^{-1}$			$\Delta G_{298K} \text{ kJ mol}^{-1}$		
		B3LYP	CBS-Q	Experiment	B3LYP	CBS-Q	Experiment
1	$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$	25.1	20.9	NA	66.7	-9.9	NA
2	$\text{SO}_3^{2-} + \text{O}_2 \rightarrow \text{O}_2 + \text{SO}_4^{2-}$	-452.8	-476.1	-416.5*	-446.4	-469.8	-421.2*
3	$\text{SO}_3^{2-} + \text{O}_2 \rightarrow \text{O} + \text{SO}_4^{2-}$	-10.1	-84.1	-24.6*	2.2	-72	-26.3*
4	$\text{HSO}_3^- + \text{OH}^* \rightarrow \text{OH}^- + \text{HSO}_3^*$	157.3	146.7	-28.2*	156.5	144.9	NA
5	$\text{HSO}_3^* + \text{O}_2 \rightarrow \text{HSO}_3^*$	-1.3	-60.7	NA	46.4	-10.9	NA
6	$\text{HSO}_3^- + \text{HSO}_3^* \rightarrow \text{HSO}_3^* + \text{HSO}_3^-$	54.8	33.7	NA	53.4	28.1	NA
7	$\text{HSO}_3^- + \text{HSO}_3^- + \text{H}^+ \rightarrow 2\text{SO}_4^{2-} + 3\text{H}^+$	697.5	639.6	NA	640.1	582.8	NA
8	$\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{SO}_3^{2-} + \text{H}_3\text{O}^+$	1270.4	1265.8	NA	1270.4	1264.8	NA
9	$\text{HCHO} + \text{HSO}_3^- \rightarrow \text{HOCH}_2\text{SO}_3^-$	361.1	332.8	NA	411.1	379.7	NA
10	$\text{HCHO} + \text{SO}_3^{2-} + \text{H}^+ \rightarrow \text{HOCH}_2\text{SO}_3^-$	-276.9	-306.9	NA	-194.1	-226.6	NA

Table 2: Continued

S/no	Aqueous phase reactions	$\Delta H_{298K} \text{ kJ mol}^{-1}$			$\Delta G_{298K} \text{ kJ mol}^{-1}$		
		B3LYP	CBS-Q	Experiment	B3LYP	CBS-Q	Experiment
11	$\text{HOCH}_2\text{SO}_3^- + \text{OH}^- \rightarrow \text{CH}_2(\text{OH})_2 + \text{SO}_3^{2-}$	-67.7	-51	NA	-153.8	-57.6	NA
12	$\text{OH}^- + \text{HOCH}_2\text{SO}_3^- \rightarrow \text{HOCHSO}_3^- + \text{H}_2\text{O}$	-476.9	-562.4	NA	-481.6	-561	NA
13	$\text{HOCH}_2\text{SO}_3^- + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{HSO}_3^- + \text{HO}_2^+$	1154.1	1177.3	NA	1146	1172.2	NA
14	$\text{O}_3 + \text{HSO}_3^- \rightarrow \text{HSO}_4^- + \text{O}_2$	-375.5	-401.4	-403.8*	-368.6	-395.3	-391.4*
15	$\text{O}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{O}_2 + \text{H}^+$	-313.4	-340.1	NA	-294	-394.3	NA
16	$\text{HSO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$	-198.9	-364.9	-366.6*	-188.6	-355.1	-351.2*
17	$\text{HSO}_3^- + \text{CH}_3\text{OOH} \rightarrow \text{HSO}_4^- + \text{CH}_3\text{OH}$	-266	-328.5	NA	-262.2	-325.2	NA
18	$\text{HSO}_3^- + \text{HOONO}_2 \rightarrow \text{HSO}_4^- + \text{NO}_3^- + \text{H}^+$	-244.8	-406.3	NA	-271.1	-431.4	NA
19	$\text{HSO}_3^- + \text{HOONO} \rightarrow \text{HSO}_4^- + \text{HNO}_2$	-89.7	-335	NA	-83.8	-329.6	NA
20	$\text{HSO}_3^- + \text{HSO}_3^- \rightarrow 2\text{HSO}_4^-$	-423.8	-490.6	NA	-414.8	-480.7	NA
21	$\text{HSO}_3^{2-} + \text{Cl}_2 \rightarrow \text{SO}_3^{2-} + 2\text{Cl}^- + \text{H}^+$	-694.2	-685.7	NA	-753.1	-739.3	NA
22	$\text{OH}^- + \text{HSO}_3^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$	-171.3	-197.8	NA	-174.1	-201.5	NA
23	$\text{OH}^- + \text{SO}_3^{2-} \rightarrow \text{SO}_3^- + \text{OH}^-$	-497.6	-511.2	NA	-496.9	-510.8	NA
24	$\text{OH}^- + \text{HSO}_3^- \rightarrow \text{SO}_3^- + \text{H}_2\text{O}$	-311.7	-297.3	NA	-315.8	-297	NA
25	$\text{OH}^- + \text{HSO}_4^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$	-83	-50.4	NA	-88	-56.1	NA
26	$\text{SO}_3^- + \text{O}_2 \rightarrow \text{SO}_3^{2-}$	-86.9	-126.5	NA	-41.9	-78.3	NA
27	$\text{SO}_5^- + \text{HSO}_3^- \rightarrow \text{HSO}_5^- + \text{SO}_3^-$	140.4	99.5	NA	141.6	95.5	NA
28	$\text{SO}_5^- + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^- + \text{H}^+$	0.1	0.1	NA	0.1	0.1	NA
29	$\text{SO}_5^- + \text{SO}_3^{2-} + \text{H}^+ \rightarrow \text{HSO}_5^- + \text{SO}_3^-$	-497.6	-540.2	NA	-463.6	-510.8	NA
30	$\text{SO}_5^- + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^-$	-272.4	-318.3	NA	-264.8	-314.3	NA
31	$\text{SO}_5^- + \text{SO}_3^- \rightarrow 2\text{SO}_4^- + \text{O}_2$	-19.9	30.3	NA	-59.1	-16.2	NA
32	$\text{SO}_5^- + \text{HO}_2^+ \rightarrow \text{HSO}_5^- + \text{O}_2$	33.8	3	NA	41.9	6.8	NA
33	$\text{SO}_5^- + \text{O}_2 + \text{H}^+ \rightarrow \text{HSO}_5^- + \text{O}_2$	-550.2	-155.6	NA	514.9	-125.3	NA
34	$\text{SO}_4^- + \text{HSO}_3^- \rightarrow \text{HSO}_4^- + \text{SO}_3^-$	-88.4	-147.4	NA	-86.1	-145.4	NA
35	$\text{SO}_4^- + \text{O}_2^- \rightarrow \text{SO}_4^{2-} + \text{O}_2$	-218.3	162.5	NA	-214.7	165.6	NA
36	$\text{SO}_4^- + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^-$	-165.7	-222.1	NA	-163.9	-219.9	NA
37	$\text{SO}_4^- + \text{NO}_3^- \rightarrow \text{SO}_4^{2-} + \text{NO}_3$	539.2	508.9	NA	537	513.5	NA
38	$\text{SO}_4^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{OH}^-$	331.9	289.1	NA	333.1	290.9	NA
39	$\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{OH}^-$	0.3	0.2	NA	0.2	0.2	NA
40	$\text{SO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{HSO}_4^- + \text{HO}_2^+$	44	-79.7	NA	47.2	-75.7	NA
41	$\text{SO}_4^- + \text{HCOOH} \rightarrow \text{SO}_4^- + \text{H}^+ + \text{COO}^-$	49.8	24.6	NA	18.4	-6.1	NA
42	$\text{SO}_4^- + \text{HCOO}^- \rightarrow \text{HSO}_4^- + \text{COO}^-$	-61	-100.5	NA	-59.4	-98.3	NA
43	$\text{SO}_4^- + \text{CH}_2(\text{OH})_2 + \text{O}_2 \rightarrow \text{HSO}_4^- + \text{HO}_2^+ + \text{HCOOH}$	-162.3	-212.1	NA	-85.8	-211.9	NA
44	$\text{SO}_4^- + \text{CH}_2(\text{OH})_2 + \text{O}_2 \rightarrow \text{HSO}_4^- + \text{HO}_2^+ + \text{HCHO} + \text{O}$	343	307.3	NA	381.2	269.2	NA
45	$\text{SO}_4^- + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}$	521.4	457.2	NA	522.5	459	NA
46	$\text{H}_2\text{SO}_4 + \text{NO}_3^- \rightarrow \text{HSO}_4^- + \text{HNO}_3$	-51.3	-58.4	-152.2*	-45.5	-57.5	-102.4*

*Enthalpies and free energies for the aqueous phase reactions determined from individual enthalpies of formation obtained from Yaws (1999) and Lide (2002). All reaction were obtained courtesy of Beilke (1978), Moller (1980), Britton and Clarke (1980), Viggiano *et al.* (1982), Breytenbach *et al.* (1994), Eisele and Tanner (1991), Herrmann *et al.* (2000), Warneck (1999) and Grgic and Bercic (2001)

thermodynamic properties of the species involved in the reaction. These properties include the Gibbs free energy and the enthalpy of the formation. The Gibbs free energy and enthalpy of formation are important in the analysis of chemical reactions (Yaws, 1999; Elliott and Carl, 1999; Sandler, 1999; Smith *et al.*, 2004). The change in the Gibbs free energy of reaction is determined from the standard Gibbs free energy of formation of the individual reactants and products involved in the reaction given by:

$$\Delta G_{\text{rxn}} = \sum \left(n \Delta G_f^0 \right)_{\text{Products}} - \sum \left(n \Delta G_f^0 \right)_{\text{Reactants}} \quad (1)$$

where, n is the number of moles of the reactants and products and

$$\Delta G_{\text{rxn}}, \left(\Delta G_f^0 \right)_{\text{Products}} \text{ and } \left(\Delta G_f^0 \right)_{\text{Reactants}}$$

are the changes in the Gibbs free of the reaction, standard free energies of the products and reactants, respectively. When $\Delta G_{\text{rxn}} < 0 \text{ kJ/mol}$, the thermodynamics of the system favours chemical reactions and if $0 < \Delta G_{\text{rxn}} < 50 \text{ kJ/mol}$, the thermodynamics of the system partially favours chemical reactions, while for $\Delta G_{\text{rxn}} > 50 \text{ kJ/mol}$, the thermodynamics for the reactions are not favourable (Yaws, 1999; Elliott and Carl, 1999; Sandler, 1999; Smith *et al.*, 2004). This change is important because it affects the chemical equilibrium for the reaction as expressed in Eq. (2) (Yaws, 1999).

$$K_{298K} = \exp \left[- \frac{\Delta G_{\text{Rxn}}}{RT} \right] \quad (2)$$

where, K_{298K} , R (kJ/mol.K) and T(K) are the equilibrium constant at 298K, gas constant and the ambient temperature. Simplifying Eq. (2) with T equals 298K, gives

$$K_{298K} = \exp[-0.4036 \Delta G_{Rxn}] \quad (3)$$

Equation (3) describes the relationship of equilibrium constant to the free energy of reaction at 298K. In a similar manner, the change in the enthalpy of a reaction, which gives the heating and cooling requirements of the system, is determined from the standard enthalpy of formation of the individual reacting species as:

$$\Delta H_{rxn} = \sum (\Delta H_f^0)_{Products} - \sum (\Delta H_f^0)_{Reactants} \quad (4)$$

where, n is the number of moles of the reactants and products

$$\Delta H_{rxn}, (\Delta H_f^0)_{Products} \text{ and } (\Delta H_f^0)_{Reactants}$$

are the changes in the enthalpy of the reaction, standard enthalpies of the products and reactants, respectively. If $\Delta H_{rxn} < 0$ kJ/mol, cooling is required to maintain reaction temperature, while for $\Delta H_{rxn} > 0$ kJ/mol, heating is required to perform the reaction (Yaws, 1999; Elliott and Carl, 1999; Sandler, 1999; Smith *et al.*, 2004). Based on the assumption of a constant change in the enthalpy of reaction within the specified temperature range, the equilibrium constant can be predicted at temperatures other than 298K (Yaws, 1999; Elliott and Carl, 1999; Sandler, 1999; Smith *et al.*, 2004; Levenspiel, 1999; Satterfield, 1991). From thermodynamics, according to the Van't Hoff expression (Smith *et al.*, 2004; Levenspiel, 1999; Satterfield, 1991) the rate of change of the equilibrium constant is given by:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_{Rxn}}{RT^2} \quad (5)$$

Integrating and simplifying Eq. 5 gives

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_{Rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

or

$$K_{T(K)} = K_{298K} \cdot \exp \left[-\frac{\Delta H_{Rxn}}{8.314 \times 10^{-3}} \left(\frac{1}{T(K)} - \frac{1}{298} \right) \right] \quad (7)$$

At equilibrium, the ratio of the product concentration to that of the reactant equals the equilibrium constant, (Levenspiel, 1999; Satterfield, 1991) that is:

$$K_{T(K)} = \frac{C_{Product}}{C_{Reactant}} = \frac{C_{PE}}{C_{RE}} \quad (8)$$

However, at any given time, the concentration of the limiting reactant at equilibrium C_{RE} is related to conversion as:

$$C_{RE} = C_{R0}(1 - X_{RE}) \quad (9)$$

And that of the desired product at equilibrium C_{PE} as a function of the limiting reactant is expressed as:

$$C_{PE} = C_{R0} X_{RE} \quad (10)$$

Then at equilibrium, the conversion of the limiting reactant is related to the operating temperature through the equilibrium constant relationship given as:

$$K_{T(K)} = \frac{C_{R0}(X_{RE})}{C_{R0}(1 - X_{RE})} = \frac{X_{RE}}{1 - X_{RE}} \quad (11)$$

where, C_{R0} and X_{RE} are the initial concentration and equilibrium conversion of the limiting reactant. Simplifying Eq. 11 gives,

$$X_{RE} = \frac{K_{T(K)}}{1 + K_{T(K)}} \quad (12)$$

Equation (11) shows that the equilibrium conversion is only dependent on the equilibrium constant. The expression implies higher the equilibrium constant, results in larger equilibrium conversion, hence the likelihood of a reaction attaining equilibrium which consequently results in a reversible reaction. As the equilibrium constant decreases with temperature the equilibrium conversion reduce and this drifts the reaction away from reaching equilibrium (Elliott and Carl, 1999; Sandler, 1999; Smith *et al.*, 2004).

MATERIALS AND METHODS

In the light of unavailable thermo chemical data from experimental observation from literature for all the species considered, the theoretical model chemistry characterised by the combination of theoretical procedure and basis set was used to produce an approximate solution to the Schrödinger equations. This was because the laws of Quantum mechanics that energy and other related properties of a molecule may be obtained by solving the Schrödinger equation. All computations were performed using *ab initio* and density functional theory methods (Grant, 1995; Hirst, 1990; Jensen, 1999) for the various species involved in the reactions as implemented in Gaussian 03 (G03) quantum chemistry package (Frisch *et al.*, 2004). Energy computations were done at

the B3LYP/6-311+G (2d,p) level for the purpose of comparison, calculations were done with 4 high energy accuracy level. A number of higher accurate energy computational methods exist. These include the DFT methods which are similar to the *ab initio* methods in computational cost and time and the compounded methods which are composed of several component calculations of *ab initio* method whose results are then combined in a pre-defined way. These are compounded computational methods i.e. the Gaussian 1 (G1), Gaussian 2 (G2), Gaussian 3 (G3), complete basis set (CBS-4) and quadratic configuration interaction (CBS-Q) theoretical levels. Each molecular structure and molecular geometry for a particular molecule was obtained with the GaussView chemistry package and structures were initially optimized at HF/3-21G* level. Subsequent optimizations of the molecular geometry for a potential energy surface were evaluated by the compounded methods. The Cartesian coordinates of the optimized molecular geometry, together with the charge and multiplicity of the compound and the computational method were used as input for the G03.

RESULTS AND DISCUSSION

The level of accuracy of the various molecular orbital computational model chemistries in relation to experimentally determined values was determined (Fig. 1) for calculated energies of reaction. All the computed energies were in the Hartree which is the default energy unit from G03 calculations. The values were converted into SI units for subsequent analysis as:

$$1 \text{ Hartree} = 2625.57 \text{ kJ mol}^{-1} \quad (13)$$

The CBS-Q method produced the highest number of computed energies of reaction that closely approximate the experimentally determined energies of reaction with a mean absolute deviation of 1.08%. This closely agrees with the expected output for the CBS-Q method from other studies (Foresman and Frisch, 1996) and hence the energies generated by the CBS-Q method in this study were presumed as approximately equal to their corresponding (if available) experimentally determined values. Consequently all the energies computed with the CBS-Q method were applied for the evaluation of the equilibrium relationships for all the reactions. The term None was used to denote computed energies that were off the experimental energies with values greater than $\pm 5\%$.

In a comparison with past works calculated energies (Maulitz *et al.*, 1995; Morgan *et al.*, 1997) for some simple anions computed with *ab initio* method MP2 at the 6-31 G (d,p) and QCISD levels as well as calculations for water

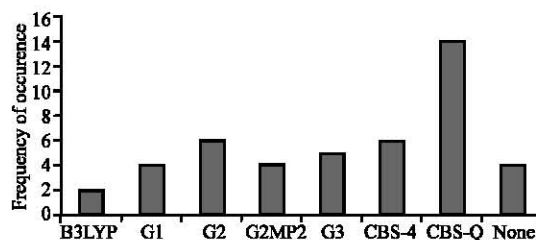


Fig. 1: Comparison of the various computational methods' level of accuracy using the determined enthalpies of reaction with the experimentally determined values as the reference energies

and some carbon based molecules (Dunbar and Petrie, 2005), at the B3LYP/6-311+G** levels and calculations for some radical species (Khachatryan *et al.*, 2004), at the B3LYP/6-31G(d,p) yielded values which closely agreed with calculated B3LYP/6-311+G(2df,p) level values shown in Table 1 and 2, some of the enthalpies and Gibbs free energies of reaction are in agreement with values for a variety of diatomic sulphur molecules computed at the B3LYP level (McKee, 1996).

Temperature effect on equilibrium constant: The equilibrium constants were calculated to provide a criterion for thermodynamically characterizing an order or preference of occurrence of a reaction against the other reactions over a particular temperature range (Fig. 2 and 3). The higher the equilibrium constant, the less stable the limiting reactant i.e. the more likely its transformation and the more its equilibrium conversion tends to unity leaving no provision for reversibility. Figure 3a-d show the temperature dependencies on the varieties of gas-phase, while the aqueous-phase sulphur reactions are illustrated in Fig. 3a-d. A number of the reactions are consistently reducing in equilibrium constant with increasing temperature at different rates while some of the set of reactions were increasing with temperature rise also at different rates. It could be seen in these figures, that similar limiting reactants involved with the same co-reactants yielding different products at equilibrium, respond to temperature changes at different rate. Also, similar limiting reactants with different co-reactants respond to temperature changes at different rate. In order to ascertain the most and possibly least relevant reactions, the equilibrium constant temperature relationships were arranged in a descending order as in Fig. 4 and 5. This arrangement shows the highest to lowest thermodynamically favourable reactions over tropospheric temperature range between -50°C and $+50^{\circ}\text{C}$ which are possibly attained in the Antarctic region and dead valley of USA, respectively. From this analysis

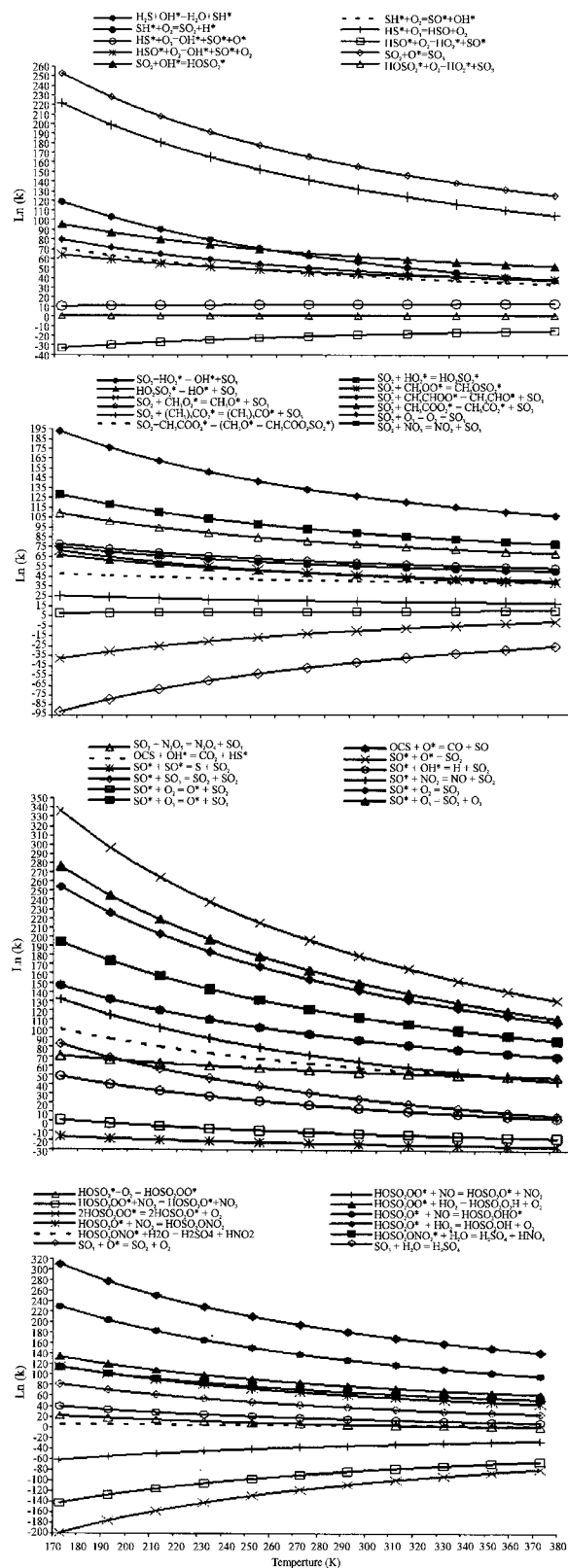


Fig. 2: Effect of ambient temperature on equilibrium for the gas-phase sulphur reactions shown in the legend

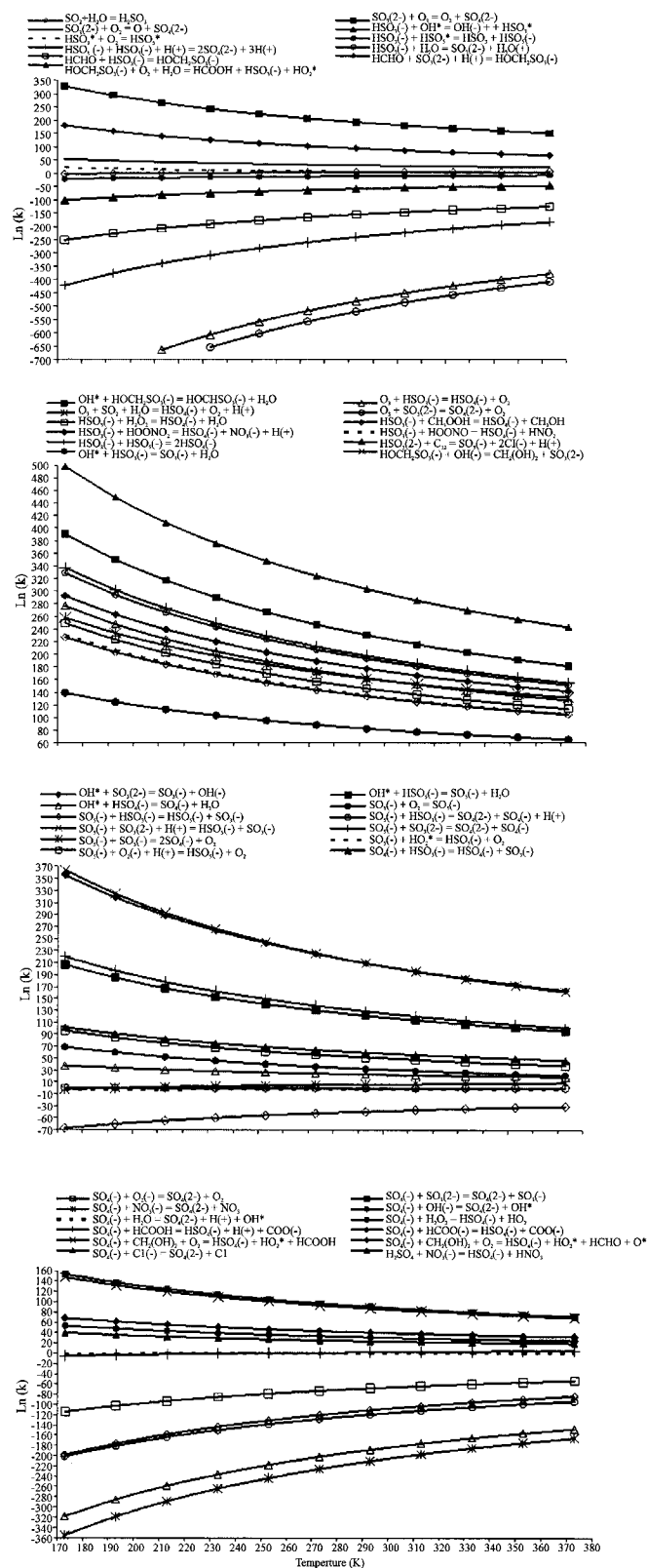


Fig. 3: Effect of ambient temperature on equilibrium for the aqueous-phase sulphur reactions shown in the legend

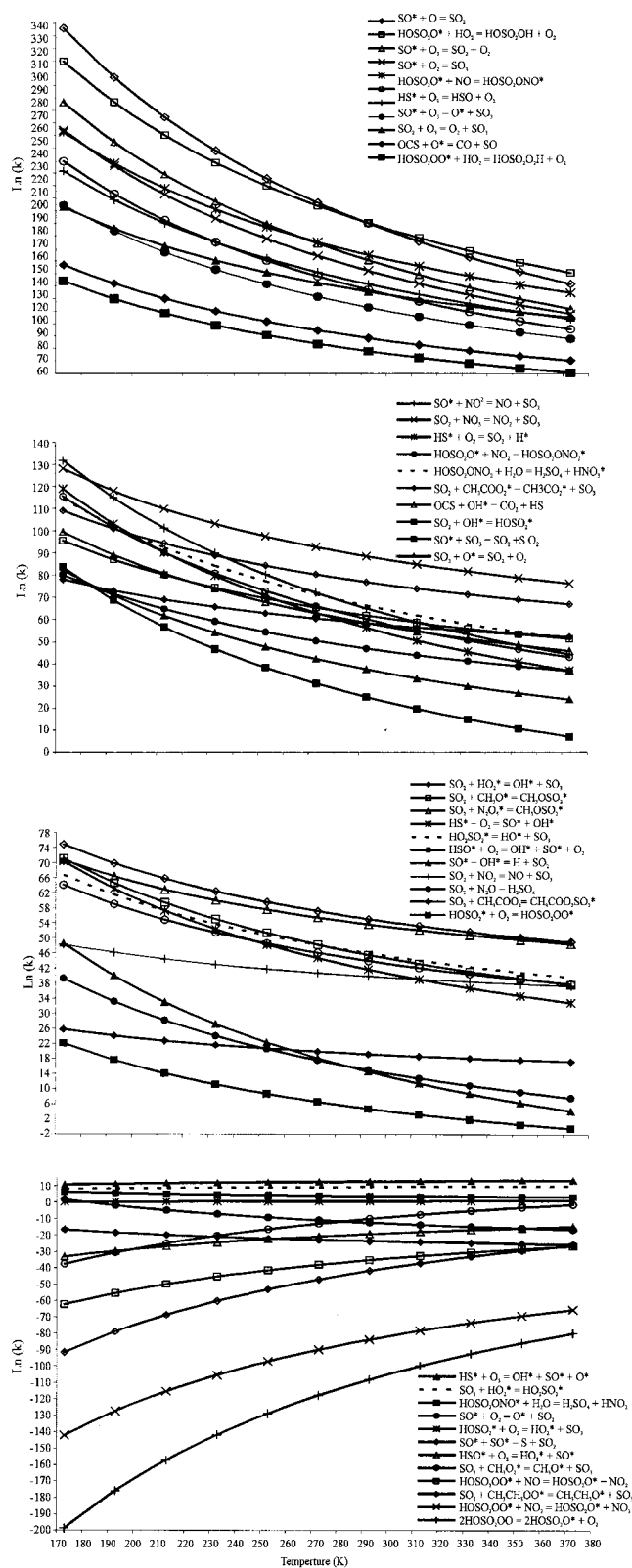


Fig. 4: The relative importance of the gas-phase atmospheric sulphur reactions from thermochemical analyses shown in the legend

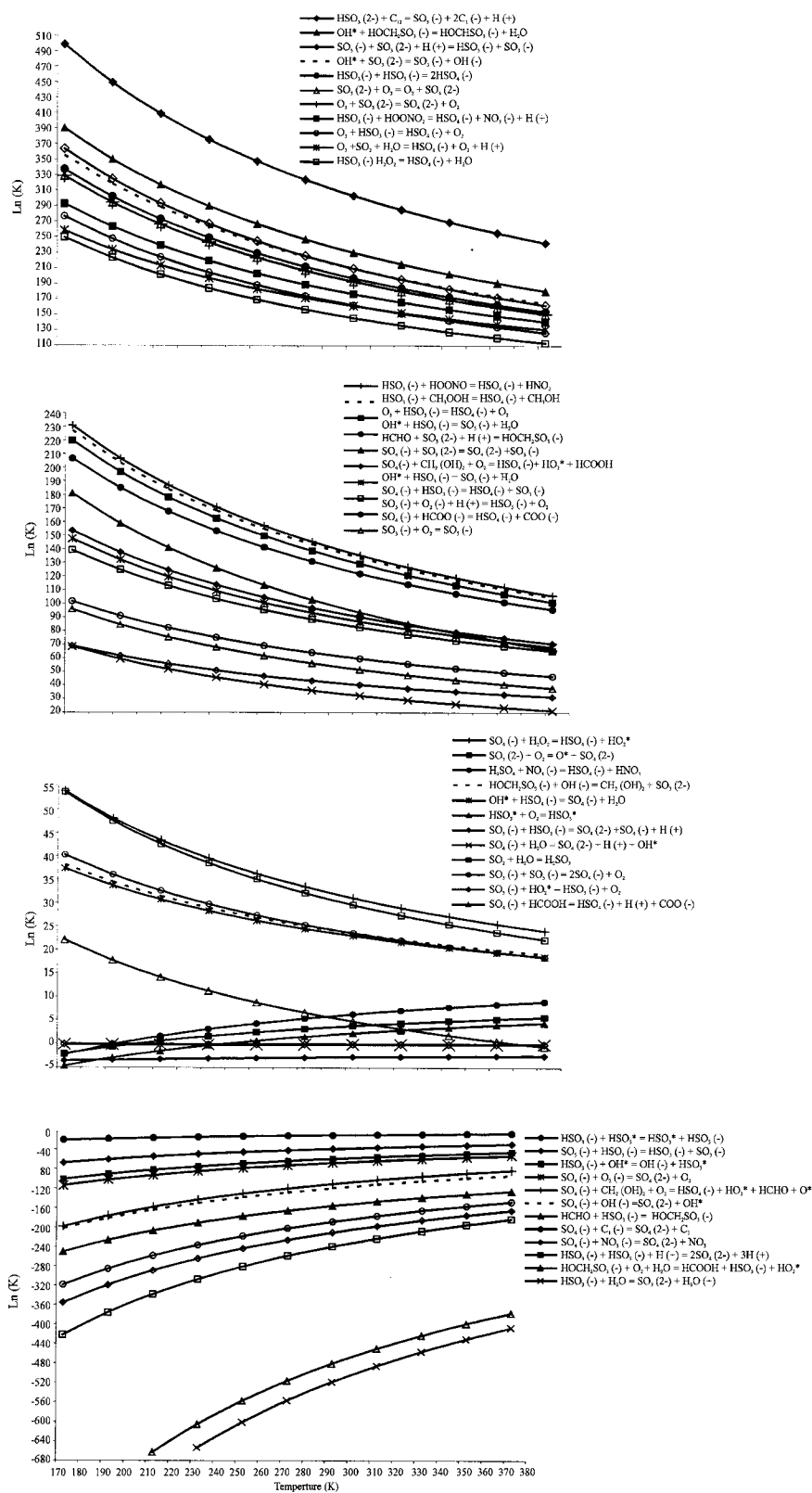


Fig. 5: The relative importance of the aqueous-phase atmospheric sulphur reactions from thermochemical analyses shown in the legend

there was one discrepancy with order arrangement of reactions (8), (9), (11) and (15) from Table 1, involving the readily occurring gas-phase reactions (Calvert *et al.*, 1978; Pienaar and Helas, 1996). An earlier order of the relative importance of SO₂ as a function of the reaction rate constant is of the form (9), (8), (11) and (15) (Warneck, 1999; Calvert *et al.*, 1978; Pienaar and Helas, 1996), while from a thermodynamics perspective it is of the form (8), (9) and (11) and (15). The latter determines the importance of the sets of reactions based on the favourability of the reaction occurring. Hence, it provide an avenue for predicting the possible products at any given ambient temperature while accounting for reversibility of the reaction yielding the forward reaction products at certain temperature and the reverse at other temperatures. The earlier approach only determines how fast a reaction occurs relative to other possibly competing reactions without the consideration of the potential favourable conditions of both reactions.

Equilibrium conversion over tropospheric temperature range: Over the extreme temperature range of between -100 and +100°C proposed as the worse scenarios of the ambient temperatures in the planetary boundary layer in different regions, about 15 and 23.4% of the gas-phase and aqueous-phase reactions in Table 1, are favoured by the forward reactions since they are most unlikely to attain equilibrium as their equilibrium conversion obtained from Eq. 12 do not approach unity over the specified temperature reactions. Consequently the expected products within the troposphere should consist only of the forward reaction. However about 80 and 59.6% of the gas-phase and aqueous-phase reactions will most likely attain equilibrium over the temperature ranging between -100 and +100°C. This implies that at certain temperatures it is most likely that the forward reaction dominates while at other temperature the reverse reaction dominates. With these sets of reactions the ambient temperature is a significant factor for predicting the potential sulphur product species of the oxidation. The balance of about 5 and 17% of the gas-phase and aqueous-phase reactions may attain equilibrium at higher temperatures above 20°C.

In winter season which is characterized by very low daytime ambient temperatures will most likely favour only the forward reactions following gas-phase reactions (6), (10), (15), (16), (27), (31), (35), (37) and (39) as well as the aqueous-phase reactions (1), (4), (6), (7), (8), (9), (13), (27), (28), (31), (32), (35), (37), (38), (39), (41), (44) and (45). This is because their equilibrium conversion is far from reaching unity.

All the reactions with positively large equilibrium constant are most likely reversible at some temperatures while irreversible at other temperature while those with

negatively large equilibrium constants are most unlikely to be reversible and thereby favoured by only the forward reactions. Reaction (5) is favoured by the forward reaction up till 80°C after which the reverse reaction occurs since equilibrium conversion is less than 0.4. Also reactions (30) and (31) are only favourable in the reverse direction since its equilibrium conversion is zero in the forward reaction. And reaction (42) is favoured by the forward reaction between -100 and -60°C and between 0 and +100°C while between -60 and 0°C it is favoured by the reverse reaction with less than 0.3 equilibrium conversion.

With the aqueous phase reactions over the temperature range about 81% are fully favoured by the forward reactions and reactions (2), (10), (12), (40), (41), (43) and (44) are only favourable in the reverse direction since its equilibrium conversion is zero in the forward reaction. And reaction (21) is favoured by the forward reaction between -100 and -90°C, while between -90 and +100°C it is favoured by the reverse reaction with zero equilibrium conversion. Also reaction (24) is partially favoured by the forward reaction over the given temperature range with equilibrium conversion equals 0.6.

Dominant atmospheric sulphur reactions: In Fig. 4a and 5a, the largest of the gas-phase and aqueous-phase equilibrium constant with temperatures are shown. In Fig. 5a, several aqueous-phase atmospheric sulphur reactions involving, HSO₃²⁻, HOCH₂SO₃⁻, SO₅⁻, SO₃⁻ are highly preferred thermodynamic reactions over the given temperature range since they poses the highest computed equilibrium constants and conversions while the first of the gas-phase reaction next in the order of preferred reactions is that involving SO⁺ (Fig. 4a). This confirms the observations previous studies (Warneck, 1999; Herrmann *et al.*, 2000; Pienaar and Helas, 1996; Moller, 1980), that aqueous phase reactions predominate and are the most essential atmospheric reaction mechanisms of SO₂ oxidation.

CONCLUSION

Analysis of atmospheric chemical reactions that may otherwise be experimentally difficult to establish could be achieved through the use of computational model theories. Atmospheric transformations are complex to effectively achieve actual reaction kinetics and thermochemical properties of the reaction species. The latter has been achieved for a significant number of homogeneous gas-phase and aqueous-phase atmospheric sulphur reactions including the intermediates and end-product with the use of molecular model computational chemistry approach of G03, to calculate electronic energies. The electronic energy was computed based on

the geometry configuration of the species molecules at 0 and 298K utilizing the electronic properties (consisting of its electronic charge and spin multiplicity) of the atoms within the particular species. The computed energies gave rise to values used in the evaluation of the thermodynamically favourable reaction pathways over ambient tropospheric temperatures. Of all the seven high-level energy accuracy method, the CBS-Q method yielded the most energies values that were approximately equal to the experimentally determined enthalpies and Gibbs free energies of reactions. This CBS-Q method predictions in contrast with energy values in literature produced a mean absolute deviation of 1.08%. Several relevant pathways for the transformation of both the gas-phase and aqueous-phase were also established with the aqueous phase dominating the reactions for SO₂ oxidation with variation over an extensive ambient temperature range of between -50 and +50°C. Over the same temperature range, about 80 and 59.6% of the gas-phase and aqueous-phase reactions, respectively were favoured towards equilibrium. Whilst about 15 and 23.4% are unlikely to attain equilibrium and finally about 5 and 17% are likely to attain equilibrium mostly at temperatures above 20°C. Over these evaluation, the common oxidising species involved in the gas-phase reactions of atmospheric SO₂ oxidation are characterized in an order of increasing oxidant's potentials in the form CH₃O₂* < HO₂* < OH* < O*.

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APPENDIX

The mean absolute deviation (MAD) of the enthalpies of reaction between CBS-Q values and Experimental Values which was used to deduce the validity of the accuracy of the CBS-Q method was determined as follows:

MAD for CBS-Q enthalpy values

$$\begin{aligned} &= \left| \overline{\Delta H}_{\text{Calc.}} - \overline{\Delta H}_{\text{Expt.}} \right| \\ &= \left| (-73.1768) - (-78.2887) \right| \\ &= 5.112 \end{aligned}$$

where, $\overline{\Delta H}_{\text{Expt.}}$ is the mean enthalpy change obtained using experimental data from literature, while $\overline{\Delta H}_{\text{Calc.}}$ is the mean enthalpy change obtained using computational model values. Therefore, as a fractional expression, the % MAD for enthalpy of reaction determined with the CBS-Q method is 1.08%.

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