

15.2.6 Oxoacids of sulfur

Sulfur, like nitrogen and phosphorus, forms many oxoacids though few of these can be isolated as the free acid and most are known either as aqueous solutions or as crystalline salts of the corresponding oxoacid anions. Sulfuric acid, H_2SO_4 , is the most important of all industrial chemicals and is manufactured on an enormous scale, greater than for any other compound of any element (p. 407). Other compounds, such as thiosulfates, sulfites, disulfites and dithionites, are valuable reducing agents with a wide variety of applications. Nomenclature is somewhat confusing but is summarized in Table 15.18 which also gives an indication of the various oxidation states of S and a schematic representation of the structures. Previously claimed species such as "sulfoxylic acid" (H_2SO_2), "thiosulfurous acid" ($\text{H}_2\text{S}_2\text{O}_2$), and their salts are now thought not to exist.

Table 15.19 Some standard reduction potentials of sulfur species (25°, pH 0)

Couple	E°/V
$2\text{H}_2\text{SO}_3 + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HS}_2\text{O}_4^- + 2\text{H}_2\text{O}$	-0.082
$\text{S} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{S}$	+0.142
$\text{HSO}_4^- + 7\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{S} + 4\text{H}_2\text{O}$	0.339
$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{S} + 3\text{H}_2\text{O}$	0.449
$\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{S} + 3\text{H}_2\text{O}$	0.465
$4\text{H}_2\text{SO}_3 + 4\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{S}_4\text{O}_6^{2-} + 6\text{H}_2\text{O}$	0.509
$\text{S}_2\text{O}_6^{2-} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{SO}_3$	0.564
$\text{S}_2\text{O}_8^{2-} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{HSO}_4^-$	2.123

Many of the sulfur oxoacids and their salts are connected by oxidation-reduction equilibria: some of the more important standard reduction potentials are summarized in Table 15.19 and displayed in graphic form as a volt-equivalent diagram (p. 435) in Fig. 15.28. By use of the couples in Table 15.19 data for many other oxidation-reduction equilibria can readily be calculated. (Indeed, it is an instructive exercise to check the derivation of the numerical data

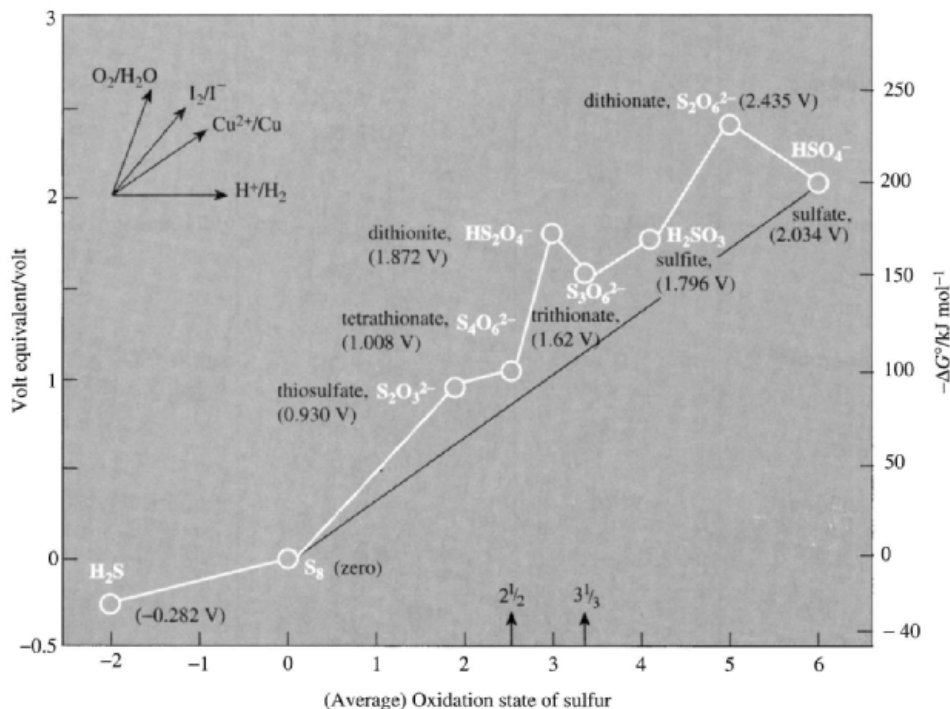
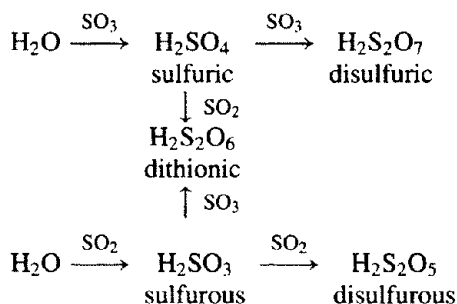


Figure 15.28 Volt-equivalent diagram for sulfur-containing species in acid solution.

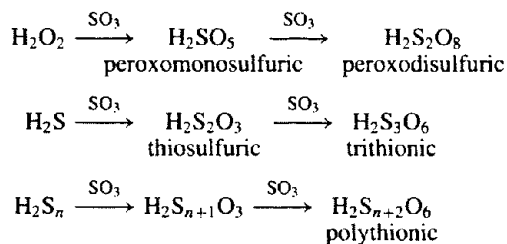
given in parentheses in Fig. 15.28 from the data given in Table 15.19 and to calculate the standard reduction potentials of other couples, e.g. $\text{HSO}_4^-/\text{H}_2\text{S}$ 0.289 V, $\text{HSO}_4^-/\text{H}_2\text{SO}_3$ 0.119 V, $\text{H}_2\text{SO}_3/\text{S}_2\text{O}_3^{2-}$ 0.433 V, etc.) Several important points emerge which are immediately apparent from inspection of Fig. 15.28. For example, it is clear that, in acid solutions, the gradient between H_2S and S_8 is less than between S_8 and any positive oxidation state, so that H_2S is thermodynamically able to reduce any oxoacid of sulfur to the element. Again, as all the intermediate oxoacids lie above the line joining HSO_4^- and S_8 , it follows that all can ultimately disproportionate into sulfuric acid and the element. Similarly, any moderately powerful oxidizing agent should be capable of oxidizing the intermediate oxoacids to sulfuric acid (sometimes with concurrent precipitation of sulfur) though by suitable choice of conditions it is often possible to obtain kinetically stable intermediate oxidation states (e.g. the polythionates with the stable S-S linkages). It follows that all the oxoacids except H_2SO_4 are moderately strong reducing agents (see below).

The formal interrelationship between the various oxoacids of sulfur can also be illustrated in a scheme⁽¹⁸⁶⁾ which places less emphasis on oxidation-reduction reactions but which is useful in suggesting possible alternative synthetic routes

to these oxoacids. Thus successive addition of SO_3 or SO_2 to H_2O can be represented by the scheme:



Likewise addition of SO_3 to H_2O_2 , H_2S and H_2S_n generates the formulae of the other oxoacids as follows:



It should be emphasized that not all the processes in these schemes represent viable syntheses, and other routes are frequently preferred. The following sections give a fuller discussion of the individual oxoacids and their salts.

¹⁸⁶ M. SCHMIDT and W. SIEBERT. Oxyacids of sulfur, Section 2.4 in *Comprehensive Inorganic Chemistry*, Vol. 2, Chapter 23, pp. 868-98, Pergamon Press, Oxford, 1973.

¹⁸⁷ R. L. KUCZKOWSKI, R. D. SUENRAM and F. J. LOVAS, *J. Am. Chem. Soc.* **103**, 2561-6 (1981).

Table 15.20 Some physical properties of anhydrous H_2SO_4 and D_2SO_4 ^(a)

Property	H_2SO_4	D_2SO_4
MP/°C	10.371	14.35
BP/°C	~300 (decomp)	—
Density(25°)/g cm ⁻³	1.8267	1.8572
Viscosity(25°)/centipoise	24.55	24.88
Dielectric constant ϵ	100	—
Specific conductivity κ (25°)/ohm ⁻¹ cm ⁻¹	1.0439×10^{-2}	0.2832×10^{-2}

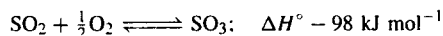
^(a)In the gas phase H_2SO_4 and D_2SO_4 adopt the C_2 conformation with r(O-H) 97 pm, r(S-OH) 157.4 pm, r(S-O) 142.2 pm; the various interatomic and dihedral angles were also determined and the molecular dipole moment calculated to be 2.73 D.⁽¹⁸⁷⁾

Industrial Manufacture of Sulfuric Acid

Sulfuric acid is the world's most important industrial chemical and is the cheapest bulk acid available in every country of the world. It was one of the first chemicals to be produced commercially in the USA (by John Harrison, Philadelphia, 1793); in Europe the history of its manufacture goes back even further — by at least two centuries.^(188,189) Concentrated sulfuric acid ("oil of vitriol") was first made by the distillation of "green vitriol", $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ and was needed in quantity to make Na_2SO_4 from NaCl for use in the Leblanc Process (p. 71). This expensive method was replaced in the early eighteenth century by the burning of sulfur and Chile saltpetre (NaNO_3) in the necks of large glass vessels containing a little water. The process was patented in 1749 by Joshua Ward (the Quack of Hogarth's *Harlot's Progress*) though it had been in use for several decades previously in Germany, France and England. The price plummeted 20-fold from £2 to 2 shillings per pound. It dropped by a further factor of 10 by 1830 following firstly John Roebuck's replacement (*ca.* 1755) of the fragile glass jars by lead-chambers of 200 ft³ (5.7 m³) capacity, and, secondly, the discovery (by N. Clement and C. B. Désormes in 1793) that the amount of NaNO_3 could be substantially reduced by admitting air for the combustion of sulfur. By 1860 James Muspratt (UK) was using lead chambers of 56 000 ft³ capacity (1585 m³) and the process was continuous. The maximum concentration of acid that could be produced by this method was about 78% and until 1870 virtually the only source of oleum was the Nordhausen works (distillation of $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$). Today both processes have been almost entirely replaced by the modern contact process. This derives originally from Peregrine Philips' observation (patented in 1831) that SO_2 can be oxidized to SO_3 by air in the presence of a platinum catalyst.

The modern process uses a potassium-sulfate-promoted vanadium(V) oxide catalyst on a silica or kieselguhr support.⁽¹⁹⁰⁾ The SO_2 is obtained either by burning pure sulfur or by roasting sulfide minerals (p. 651) notably iron pyrite, or ores of Cu, Ni and Zn during the production of these metals. On a worldwide basis about 65% of the SO_2 comes from the burning of sulfur and some 35% by the roasting of sulfide ores but in some countries (e.g. the UK) over 95% comes from the former.

The oxidation of SO_2 to SO_3 is exothermic and reversible:



According to le Chatelier's principle the *yield* of SO_3 will increase with increase in pressure, increase in excess O_2 concentration, and removal of SO_3 from the reaction zone; each of these factors will also increase the *rate* of conversion somewhat (by the law of mass action). Reaction rate will also increase substantially with increase in temperature but this will simultaneously decrease the yield of the exothermic forward reaction. Accordingly, a catalyst is required to accelerate the reaction without diminishing the yield. Optimum conditions involve an equimolar feed of O_2/SO_2 (i.e. air/ SO_2 :5/1) and a 4-stage catalytic converter operating at the temperatures shown in the Figure.⁽¹²³⁾ (The V_2O_5 catalyst is inactive below 400°C and breaks down above 620°C; it is dispersed as a thin film of molten salt on the catalyst support.) Such a converter may be 13 m high, 9 m in diameter, contain 80 tonnes of catalyst pellets and produce 500 tonnes per day of acid. The gas temperature rises during passage through the catalyst bed and is recooled by passage through external heat-exchanger loops between the first three stages. In the most modern "double-absorption" plants (IPA) the SO_3 is removed at this stage before the residual SO_2/O_2 is passed through a fourth catalyst bed for final conversion. The SO_3 gas cannot be absorbed directly in water because it would first come into contact with the water-vapour above the absorber and so produce a stable mist of fine droplets of H_2SO_4 which would then pass right through the absorber and out into the atmosphere. Instead, absorption is effected by 98% H_2SO_4 in ceramic-packed towers and sufficient water is added to the circulating acid to maintain the required concentration. Commercial conc H_2SO_4 is generally 96–98% to prevent undesirable solidification of the product. The main construction materials of the sulfur burner, catalytic converter, absorption towers and ducting are mild steel and stainless steel, and the major impurity in the acid is therefore Fe^{II} (10 ppm) together with traces of SO_2 and NO_x .

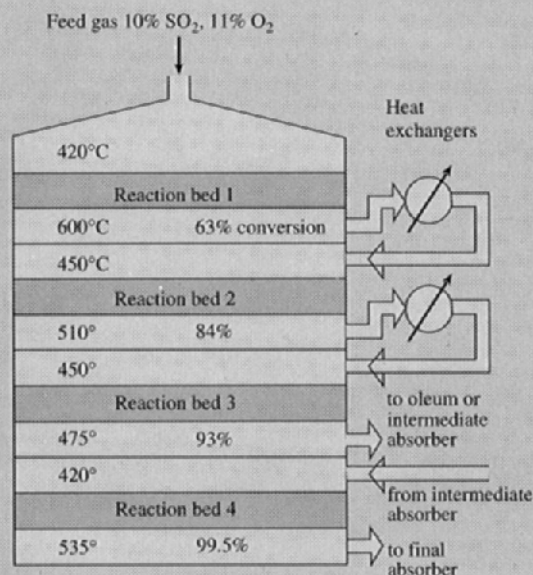
Some idea of the accelerating demand for sulfuric acid can be gained from the following UK production figures:

Year	1860	1870	1880	1890	1900	1917	1960	1980
10 ³ tonnes	260	560	900	870	1100	1400	2750	4750

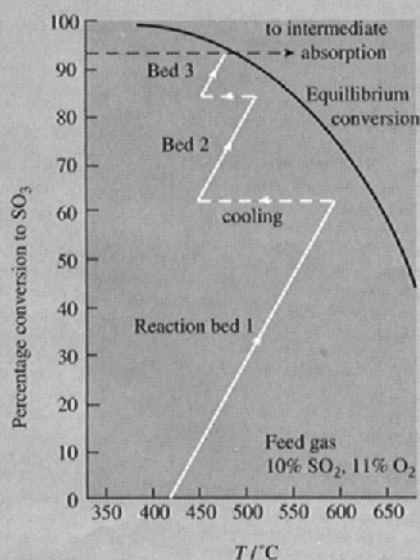
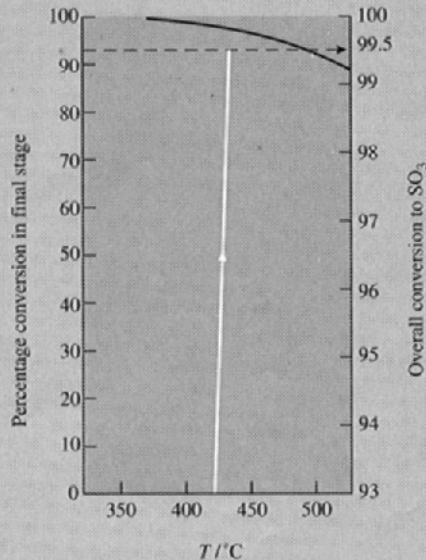
¹⁸⁸T. K. DERRY and T. I. WILLIAMS, *A Short History of Technology from the Earliest Times to AD 1900*, pp. 268, and 534–5, Oxford University Press, Oxford, 1960.

¹⁸⁹L. F. HABER, *The Chemical Industry During the Nineteenth Century*, Oxford University Press, Oxford, 1958, 292 pp; L. F. HABER, *The Chemical Industry 1900–1930*, Oxford University Press, Oxford, 1971, 452 pp.

¹⁹⁰A. PHILLIPS, in R. THOMPSON (ed.), *The Modern Inorganic Chemicals Industry*, pp. 183–200, The Chemical Society, London, 1977. See also W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH Publishers, New York, pp. 108–20 (1989).



Schematic diagram of converter

Conversion versus temperature
— first stage.Conversion versus temperature
— final stage (reaction bed 4).

Double absorption (IPA) sulfuric acid plant.

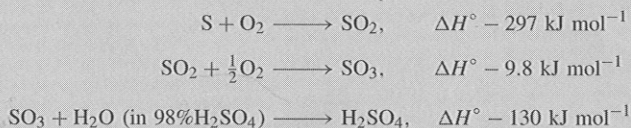
Figures for France, Germany and the USA were lower than these until the turn of the century, but then the USA began to outstrip the rest. At about the same time superphosphate manufacture overtook the Leblanc soda process as the main user of H₂SO₄. H₂SO₄ production is now often taken as a reliable measure of a nation's industrial strength because it enters into so many industrial and manufacturing processes. Thus in 1900 production was equivalent to 4.05 million tonnes of 100% H₂SO₄ distributed as follows (%):

UK	USA	Germany	France	Austria	Belgium	Russia	Japan
25.9	23.2	21.0	15.5	4.9	4.0	3.1	1.2

By 1976 world production was 113 million tonnes and the distribution changed to the following (%):

USA	USSR	Japan	Germany	France	Poland	UK	Canada	Spain	Italy	Others
25.6	17.7	5.4	4.1	3.5	3.2	2.9	2.8	2.5	2.4	29.9

This had increased to 145 million tonnes by 1986 (Europe 44%, USA/Canada 24%, Asia/Oceania 18%, Africa 9%, Latin America 5%). Such vast quantities require huge plants: these frequently have a capacity in excess of 2000 tonnes per day in the USA but are more commonly in the range 300–750 tonnes per day in Europe and smaller still in less industrialized countries. Even so, the energy flows are enormous as can be appreciated by scaling up the following reactions:



For example, the oxidation of S to SO₃ liberates nearly 4×10^9 J per tonne of H₂SO₄ of which ~3 GJ can be sold as energy in the form of steam and much of the rest used to pump materials around the plant, etc. A plant producing 750 tonnes per day of H₂SO₄ produces ~25 MW of byproduct thermal energy, equivalent to ~7 MW of electricity if the steam is used to drive generators. Effective utilization of this energy is an important factor in minimizing the cost of sulfuric acid which remains a remarkably cheap commodity despite inflation (of the order of \$150 per tonne in 1994).

Environmental legislation in the USA requires that sulfur emitted from the stack (SO₂ and persistent H₂SO₄ mist) must not exceed 0.3% of the sulfur burned (0.5% in the UK). Despite this, because of the vast scale of the industry, large quantities of unconverted SO₂ are vented to the atmosphere each year (say 0.3% of 145×10^6 tonnes $\times \frac{64}{98} = 284\,000$ tonnes SO₂ pa). It is a testament to the efficiency of the process that this represents a global impact of only some 780 tonnes SO₂ per day, which is minute compared with other sources of this pollution (p. 698).

The pattern of use of H₂SO₄ varies from country to country and from decade to decade. Current US usage is dominated by fertilizer production (70%) followed by chemical manufacture, metallurgical uses, and petroleum refining (~5% each). In the UK the distribution of uses is more even: only 30% of the H₂SO₄ manufactured is used in the fertilizer industry but 18% goes on paints, pigments and dyestuff intermediates, 16% on chemicals manufacture, 12% on soaps and detergents, 10% on natural and manmade fibres, and 2.5% on metallurgical applications.

Sulfuric acid, H₂SO₄

Anhydrous sulfuric acid is a dense, viscous liquid which is readily miscible with water in all proportions: the reaction is extremely exothermic (~880 kJ mol⁻¹ at infinite dilution) and can result in explosive spattering of the mixture if the water is added to the acid; it is therefore important always to use the reverse order and add the acid to the water, slowly and with stirring. The large-scale preparation of sulfuric acid is a major industry in most countries and is described in the preceding Panel.

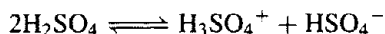
Some physical properties of anhydrous H₂SO₄ (and D₂SO₄) are in Table 15.20 (p. 707).^(191,192) In addition, several congruently melting hydrates,

H₂SO₄·*n*H₂O, are known with *n* = 1, 2, 3, 4 (mps 8.5°, -39.5°, -36.4° and -28.3°, respectively). Other compounds in the H₂O/SO₃ system are H₂S₂O₇ (mp 36°) and H₂S₄O₁₃ (mp 4°). Anhydrous H₂SO₄ is a remarkable compound with an unusually high dielectric constant, and a very high electrical conductivity which results from the ionic self-dissociation (autoprotolysis) of the compound coupled with a proton-switch mechanism for the rapid

¹⁹¹ R. J. GILLESPIE and E. A. ROBINSON, *Sulfuric acid*, Chap. 4 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 117–210, Academic Press, London, 1965. A definitive review with some 250 references.

¹⁹² N. N. GREENWOOD and A. THOMPSON, *J. Chem. Soc.* 3474–84 (1959).

conduction of current through the viscous H-bonded liquid. For example, at 25° the single-ion conductances for H_3SO_4^+ and HSO_4^- are 220 and 150 respectively, whereas those for Na^+ and K^+ which are viscosity-controlled are only 3–5. Anhydrous H_2SO_4 thus has many features in common with anhydrous H_3PO_4 (p. 518) but the equilibria are reached much more rapidly (almost instantaneously) in H_2SO_4 :



$$K_{\text{ap}}(25^\circ) = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 2.7 \times 10^{-4}$$

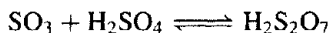
This value is compared with those for other acids and protonic liquids in Table 15.21.⁽¹⁹¹⁾ the extent of autoprotolysis in H_2SO_4 is greater than that in water by a factor of more than 10^{10} and is exceeded only by anhydrous H_3PO_4 and $[\text{HBF}_3(\text{OH})]$ (p. 198). In addition to autoprotolysis, H_2SO_4 undergoes ionic self-dehydration:



This arises from the primary dissociation of H_2SO_4 into H_2O and SO_3 which then react with further H_2SO_4 as follows:



$$K_{\text{H}_2\text{O}}(25^\circ) = [\text{H}_3\text{O}^+][\text{HSO}_4^-]/[\text{H}_2\text{O}] \sim 1$$



$$K_{\text{H}_2\text{S}_2\text{O}_7}(25^\circ) = [\text{H}_3\text{SO}_4^+][\text{HS}_2\text{O}_7^-]/[\text{H}_2\text{S}_2\text{O}_7] \\ = 1.4 \times 10^{-2}$$

It is clear that “pure” anhydrous sulfuric acid, far from being a single substance in the bulk liquid phase, comprises a dynamic equilibrium involving at least seven well-defined species. The

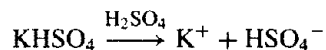
concentration of the self-dissociation products in H_2SO_4 and D_2SO_4 at 25° (expressed in millimoles of solute per kg solvent) are:

HSO_4^-	H_3SO_4^+	H_3O^+	HS_2O_7^-	$\text{H}_2\text{S}_2\text{O}_7$	H_2O	Total
15.0	11.3	8.0	4.4	3.6	0.1	42.4
DSO_4^-	D_3SO_4^+	D_3O^+	DS_2O_7^-	$\text{D}_2\text{S}_2\text{O}_7$	D_2O	Total
11.2	4.1	11.2	4.9	7.1	0.6	39.1

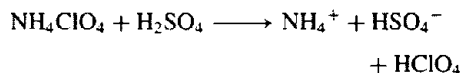
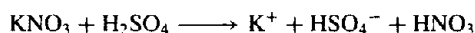
As the molecular weight of H_2SO_4 is 98.078 it follows that 1 kg contains 10.196 mol; hence the predominant ions are present to the extent of about 1 millimole per mole of H_2SO_4 and the total concentration of species in equilibrium with the parent acid is 4.16 millimole per mole. Many of the physical and chemical properties of anhydrous H_2SO_4 as a nonaqueous solvent stem from these equilibria.

In the sulfuric acid solvent system, compounds that enhance the concentration of the solvo-cation HSO_4^- will behave as bases and those that give rise to H_3SO_4^+ will behave as acids (p. 425). Basic solutions can be formed in several ways of which the following examples are typical:

- (a) Dissolution of metal hydrogen sulfates:



- (b) Solvolysis of salts of acids that are weaker than H_2SO_4 :



- (c) Protonation of compounds with lone-pairs of electrons:

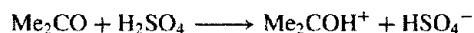
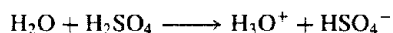
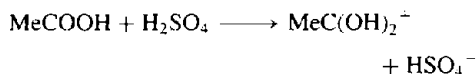
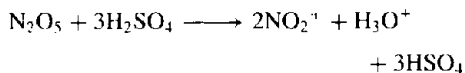
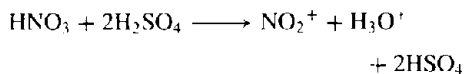


Table 15.21 Autoprotolysis constants at 25°

Compound	$-\log K_{\text{ap}}$	Compound	$-\log K_{\text{ap}}$	Compound	$-\log K_{\text{ap}}$
$\text{HBF}_3(\text{OH})$	~ -1	HCO_2H	6.2	H_2O_2	12
H_3PO_4	~ 2	HF	9.7	H_2O	14.0
H_2SO_4	3.6	MeCO_2H	12.6	D_2O	14.8
D_2SO_4	4.3	EtOH	18.9	NH_3	29.8



(d) Dehydration reactions:

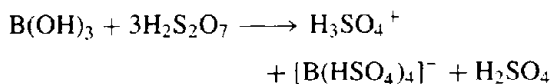


The reaction with HNO_3 is quantitative, and the presence of large concentrations of the nitronium ion, NO_2^+ , in solutions of HNO_3 , MNO_3 and N_2O_5 in H_2SO_4 enable a detailed interpretation to be given of the nitration of aromatic hydrocarbons by these solutions.

Because of the high acidity of H_2SO_4 itself, bases form the largest class of electrolytes and only few acids (proton donors) are known in this solvent system. As noted above, $\text{H}_2\text{S}_2\text{O}_7$ acts as a proton donor to H_2SO_4 and HSO_3F is also a weak acid:



One of the few strong acids is tetra(hydrogen sulfato)boric acid $\text{B}(\text{HSO}_4)_4$; solutions of this can be obtained by dissolving boric acid in oleum:



Other strong acids are $\text{H}_2\text{Sn}(\text{HSO}_4)_6$ and $\text{H}_2\text{Pb}(\text{HSO}_4)_6$.

Sulfuric acid forms salts (sulfates and hydrogen sulfates) with many metals. These are frequently very stable and, indeed, they are the most important mineral compounds of several of the more electropositive elements. They have been discussed in detail under the appropriate elements. Sulfates can be prepared by:

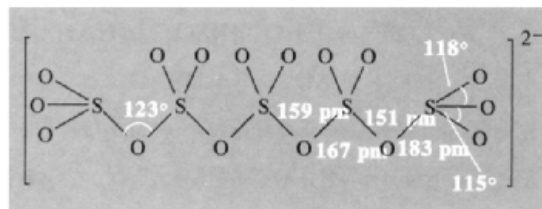
- dissolution of metals in aqueous H_2SO_4 (e.g. Fe);
- neutralization of aqueous H_2SO_4 with metal oxides or hydroxides (e.g. MOH);
- decomposition of salts of volatile acids (e.g. carbonates) with aqueous H_2SO_4 ;

(d) metathesis between a soluble sulfate and a soluble salt of the metal whose (insoluble) sulfate is required (e.g. BaSO_4);

(e) oxidation of metal sulfides or sulfites.

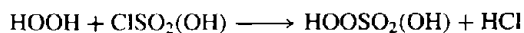
The sulfate ion is tetrahedral ($\text{S}-\text{O}$ 149 pm) and can act as a monodentate, bidentate (chelating) or bridging ligand. Examples are in Fig. 15.29. Vibrational spectroscopy is a useful diagnostic, as the progressive reduction in local symmetry of the SO_4 group from T_d to C_{3v} and eventually C_{2v} increases the number of infrared active modes from 2 to 6 and 8 respectively, and the number of Raman active modes from 4 to 6 and 9.⁽¹⁹³⁾ (The effects of crystal symmetry and the overlapping of bands complicates the analysis but correct assignments are frequently still possible.)

Pairs of corner-shared SO_4 tetrahedra are found in the disulfates, $\text{S}_2\text{O}_7^{2-}$ ($\text{S}-\text{O}_\mu-\text{S}$ 124°, $\text{S}-\text{O}_\mu$ 164.5 pm, $\text{S}-\text{O}_t$ 144 pm); they are made by thermal dehydration of MHSO_4 . Likewise the trisulfate ion $\text{S}_3\text{O}_{10}^{2-}$ is known and also the pentasulfate ion, $\text{S}_5\text{O}_{16}^{2-}$ whose structure indicates an alternation of $\text{S}-\text{O}$ interatomic distances and very long $\text{O}-\text{S}$ distances to the almost planar terminal SO_3 groups:



Peroxosulfuric acids, H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_8$

Anhydrous peroxomonosulfuric acid (Caro's acid) can be prepared by reacting chlorosulfuric acid with anhydrous H_2O_2



¹⁹³ K. NAKAMOTO, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn., Wiley, New York, 1970, 338 pp. (See also *J. Am. Chem. Soc.* **79**, 4904-8 (1957) for detailed correlation table.)