Overhead Slides for

Chapter 19

of

Fundamentals of Atmospheric Modeling

by

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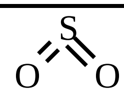
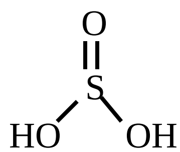
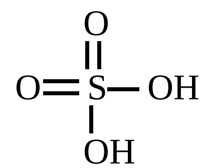
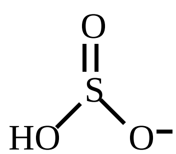
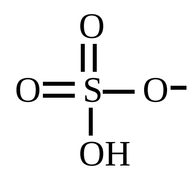
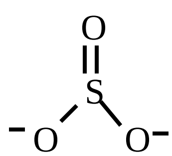
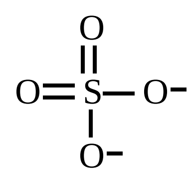
Aqueous Chemistry

Table 19.1. Names, formulae, and Lewis structures of S(IV) and S(VI) species.

S(IV) Family		S(VI) Family	
Chemical Name and Formula	Chemical Structure	Chemical Name and Formula	Chemical Structure
Sulfur dioxide (aq) SO_2(aq)			
Sulfurous acid (aq) H_2SO_3(aq)		Sulfuric acid (aq) H_2SO_4(aq)	
Bisulfite ion HSO_3^-		Bisulfate ion HSO_4^-	
Sulfite ion SO_3^{2-}		Sulfate ion SO_4^{2-}	

Aqueous Reactions in Clouds

Fig. 19.1. Comparison of cloud composition when SO_2 (a) did not and (b) did dissolve and react in the clouds.

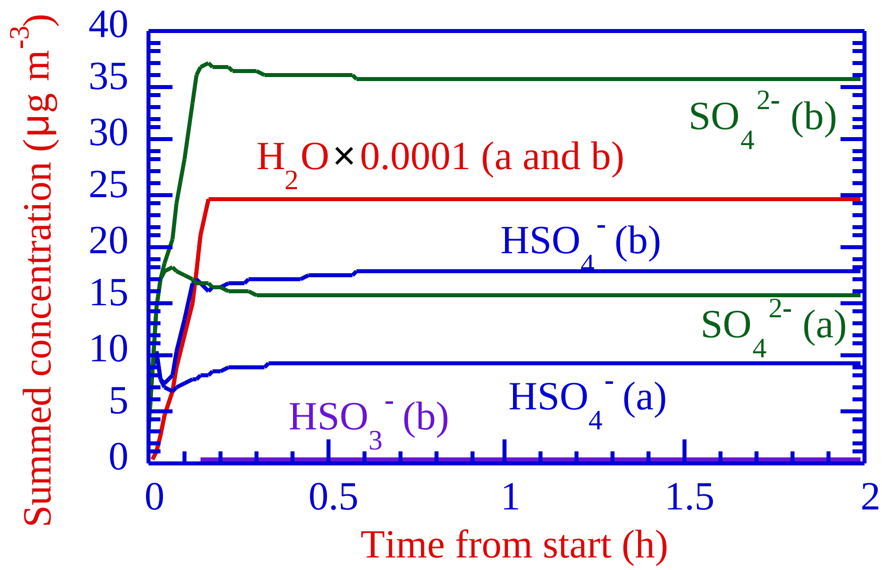
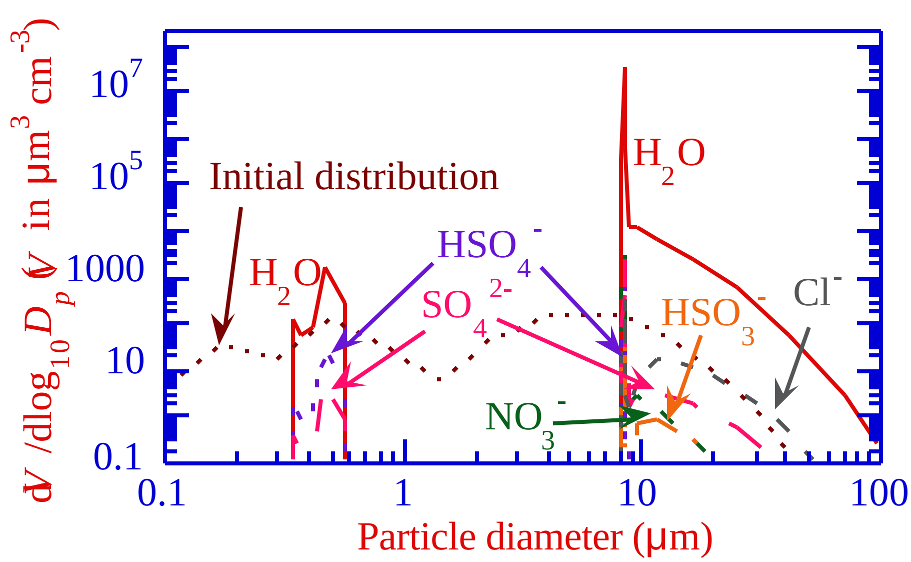
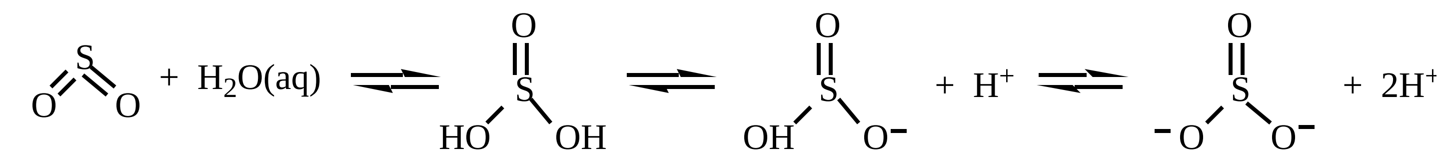


Fig. 19.2. Initial and final distribution for fig. 19.1.



Aqueous Inorganic Reactions

Sulfur dioxide dissolution and dissociation

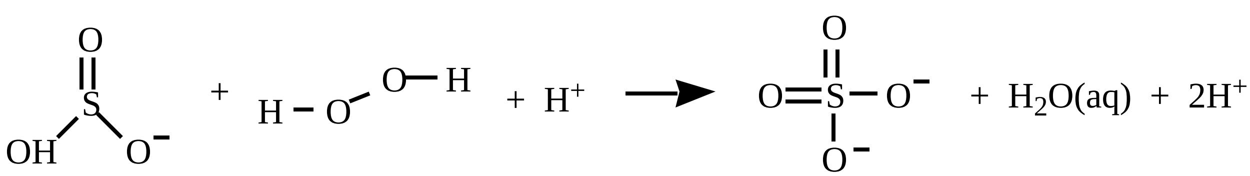


Sulfur dioxide (aq) | Sulfurous acid (aq) | Bisulfite ion | Sulfite ion

(19.2)

At pH between 2 and 7 ---> most S(IV) exists as HSO_3^-.

Conversion of S(IV) by hydrogen peroxide



Bisulfite ion | Hydrogen peroxide (aq) | Sulfate ion

(19.3)

If $[H_2O_2(aq)] > [S(IV)]$

S(IV) is consumed within tens of minutes

If $[S(IV)] > [H_2O_2(aq)]$

$H_2O_2(aq)$ is consumed within minutes

Aqueous Inorganic Reactions

Sources of hydrogen peroxide

$$H_2O_2(g) \rightleftharpoons H_2O_2(aq) \qquad (19.4)$$

$$H{-}O{-}O^{\bullet} + O_2^{-} + H_2O(aq) \longrightarrow H{-}O{-}O{-}H + O_2(aq) + OH^{-} \qquad (19.5)$$

Hydroperoxy radical (aq) → Hydrogen peroxide (aq)

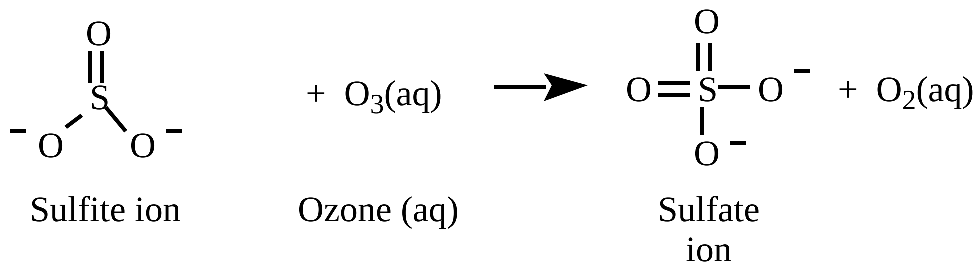
Sinks of hydrogen peroxide

$$H_2O_2(aq) + h\nu \longrightarrow 2\dot{O}H(aq) \qquad (19.6)$$

$$H_2O_2(aq) + \dot{O}H(aq) \longrightarrow H_2O(aq) + H\dot{O}_2(aq) \qquad (19.7)$$

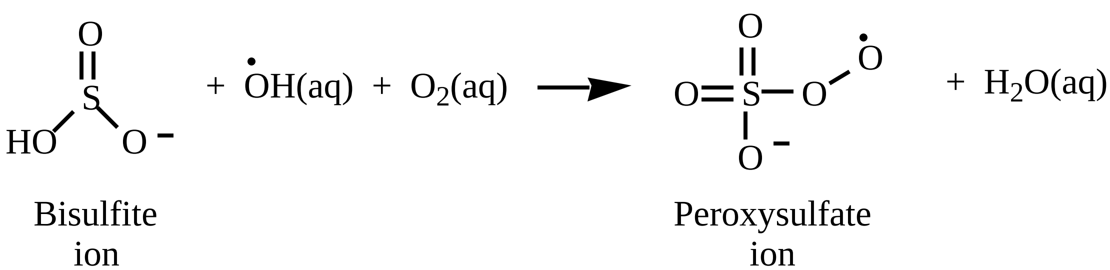
Aqueous Inorganic Reactions

Sulfite oxidation by ozone, important when pH > 6



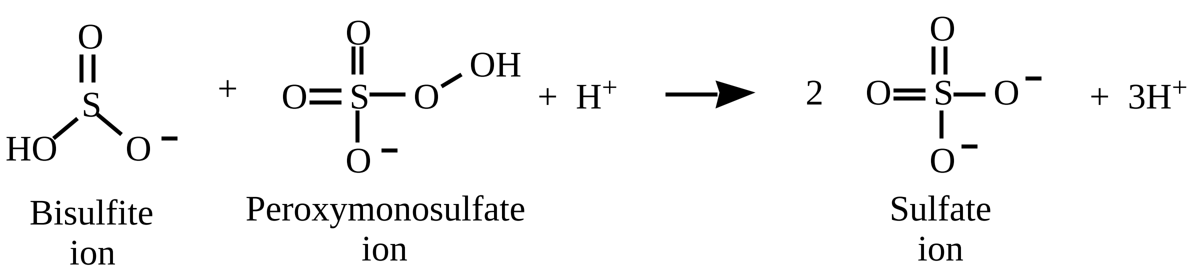
(19.8)

Bisulfite oxidation by hydroxyl, important when pH ≈ 5



(19.9)

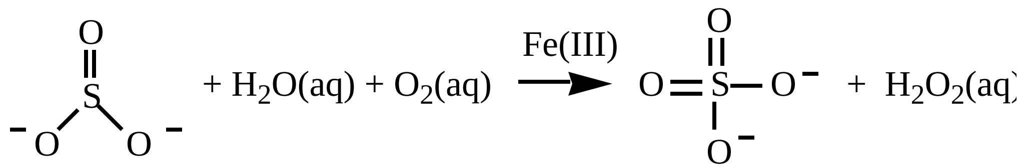
Bisulfite oxidation by peroxymonosulfate



(19.11)

Catalysis Reactions

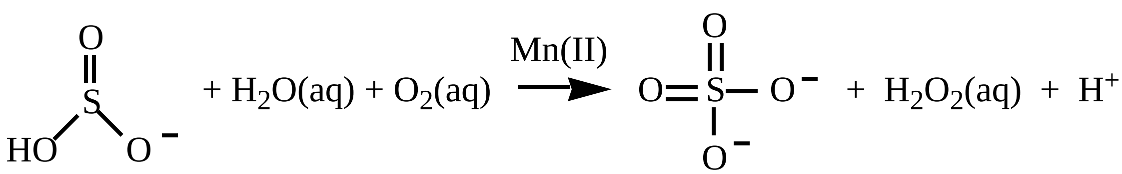
At low pH, Fe(III) = Fe^{3+}, which catalyzes S(IV) oxidation (At high pH, Fe(III) = $Fe(OH)_3(s)$, which does not)



Sulfite ion Sulfate ion

(19.12)

Mn(II) = Mn^{2+} catalyzes S(IV) oxidation

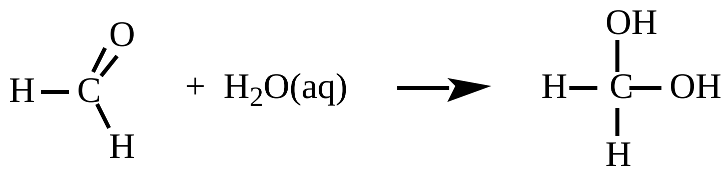


Bisulfite ion Sulfate ion

(19.13)

Organic Reactions

Formaldehyde gas dissolves then forms methylene glycol

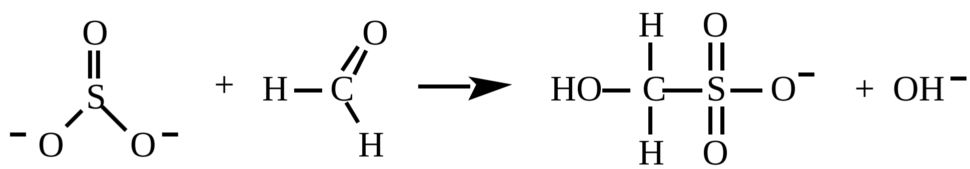


Formaldehyde (aq)

Methylene glycol (aq)

(19.14)

Formaldehyde also forms hydroxymethanesulfonate (HMSA)



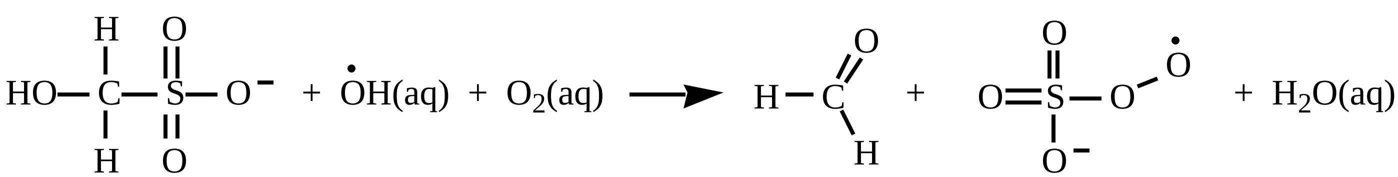
Sulfite ion

Formaldehyde (aq)

HMSA

(19.15)

HMSA lost by reaction with the hydroxyl radical



HMSA

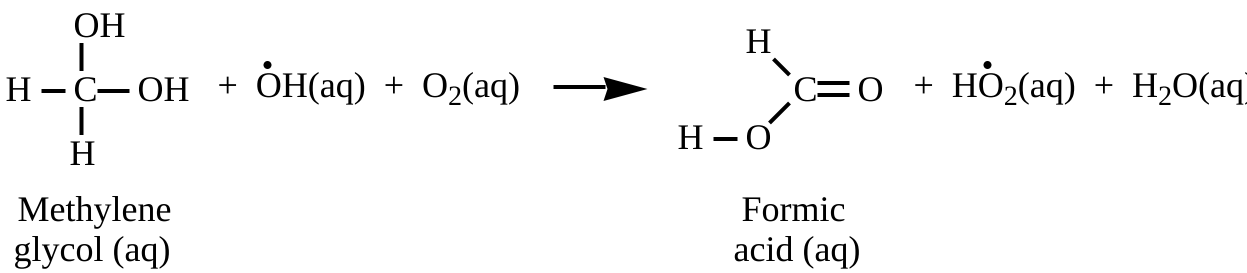
Formaldehyde (aq)

Peroxysulfate ion

(19.16)

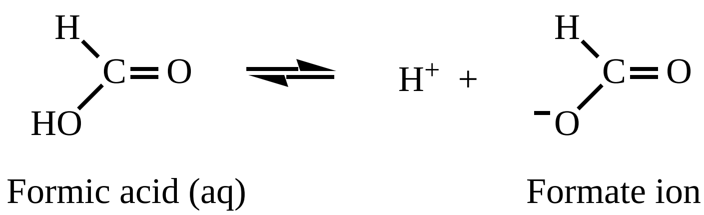
Organic Reactions

Hydroxyl radical also converts methylene glycol to formic acid



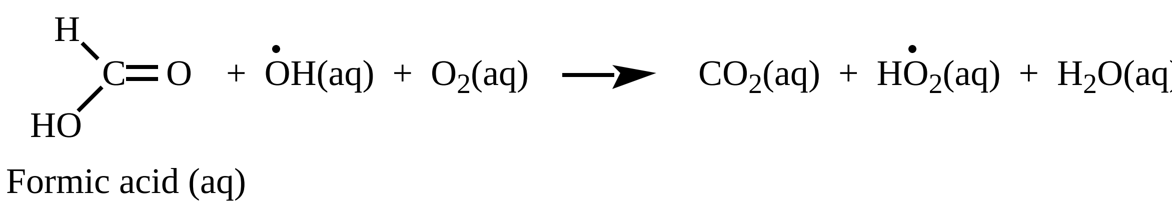
(19.17)

Formic acid dissociation to formate



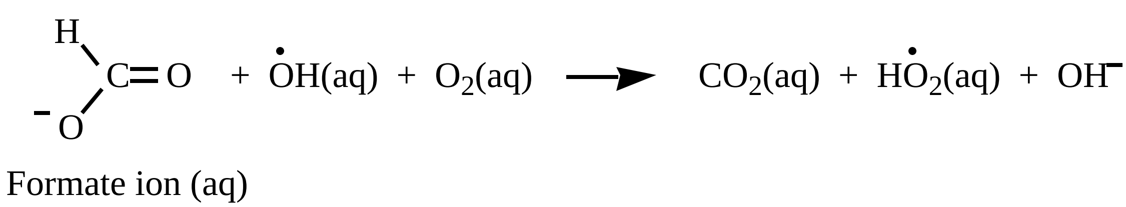
(19.18)

Formic acid oxidation by hydroxyl radical



(19.19)

Formate oxidation by hydroxyl radical



(19.20)

Halogen Reactions

Dichloride ion equilibrium with chlorine atom and chloride ion

$$Cl_2^- \rightleftharpoons \dot{Cl}(aq) + Cl^- \quad (19.21)$$

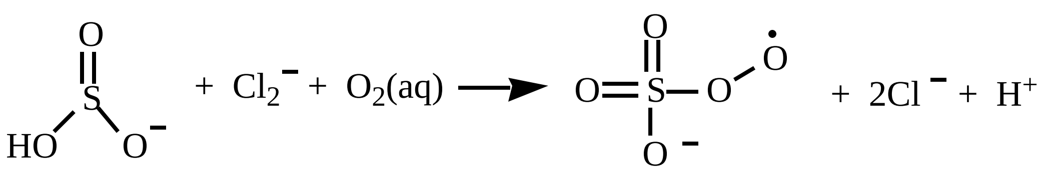
Chlorine hydroxide radical equilibrium with chloride ion and OH

$$ClOH^- \rightleftharpoons Cl^- + \dot{O}H(aq) \quad (19.22)$$

Conversion of hydrogen peroxide by chlorine atom

$$H_2O_2(aq) + \dot{Cl}(aq) \longrightarrow Cl^- + H\dot{O}_2(aq) + H^+ \quad (19.23)$$

Dichloride ion conversion of bisulfite --> peroxysulfate



Bisulfite ion

Peroxysulfate ion

Diffusion Within a Drop

Characteristic time for aqueous phase diffusion

$$\tau_{ad,q} = \frac{r_i^2}{\pi^2 D_{aq,q}} \qquad (19.25)$$

Example 19.1.

	d_i	= 30 μm
--->	$\tau_{ad,q}$	= 0.05 s
	d_i	= 10 μm
--->	$\tau_{ad,q}$	= 0.001 s

Reaction times for $O_3(aq)$, $NO_3(aq)$, $OH(aq)$, $Cl(aq)$, SO_4^- CO_3^-, and Cl_2^- are shorter than diffusion transport times

Time rate of change of concentration of species *q* in size bin *i* as a function of radius during diffusion

$$\left(\frac{dc_{q,i,r}}{dt}\right)_{ad,aq} = D_{aq,q}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{q,i,r}}{\partial r}\right) + P_{c,q,i,r} - L_{c,q,i,r} \qquad (19.26)$$

Boundary condition

- At drop center, $\partial c_{q,i,r} / \partial r = 0$

Coupling Aqueous Chemistry to Growth and Equilibrium

Aqueous reactions stiffer than gas reactions

Aqueous reactions solved in more size bins than gas reactions

Aqueous concentrations strongly coupled to growth and equilibrium

- Either time split aqueous chemistry from other processes with a small splitting time step
- or solve aqueous chemistry together with other processes

Change in aerosol composition

$$\left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{ge,eq,aq} = \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{ge} + \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{eq} + \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{aq} \tag{19.27}$$

Corresponding conservation of gas equation

$$\frac{\mathrm{d}C_{q,t}}{\mathrm{d}t} = -\sum_{i=1}^{N_B}\left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{ge} \tag{19.28}$$

Aqueous Families

$$c_{S(IV),i} = c_{SO_2(aq),i} + c_{HSO_3^-,i} + c_{SO_3^{2-},i} \quad (19.29)$$

$$c_{S(VI),i} = c_{H_2SO_4(aq),i} + c_{HSO_4^-,i} + c_{SO_4^{2-},i} \quad (19.30)$$

$$c_{HO_{2,T},i} = c_{HO_2(aq),i} + c_{O_2^-,i} \quad (19.31)$$

$$c_{CO_{2,T},i} = c_{CO_2(aq),i} + c_{HCO_3^-,i} + c_{CO_3^{2-},i} \quad (19.32)$$

$$c_{HCHO_T,i} = c_{HCHO(aq),i} + c_{H_2C(OH)_2,i} \quad (19.33)$$

$$c_{HCOOH_T,i} = c_{HCOOH(aq),i} + c_{HCOO^-,i} \quad (19.34)$$

$$c_{CH_3COOH_T,i} = c_{CH_3COOH(aq),i} + c_{CH_3COO^-,i} \quad (19.35)$$

Aqueous Families

Change in S(VI) concentration due to growth, aqueous chemistry

$$\frac{\mathrm{d}c_{\mathrm{S(IV)},i}}{\mathrm{d}t} = k_{\mathrm{S(IV)},i}\left(C_{\mathrm{SO_2(g)}} - S'_{\mathrm{S(IV)},i}\frac{c_{\mathrm{SO_2(aq)},i}}{H'_{\mathrm{SO_2(aq)},i}}\right) + P_{c,\mathrm{S(IV)},i} - L_{c,\mathrm{S(IV)},i}$$

(19.36)

Chemical production and loss terms

$$P_{c,q,i,t} = \sum_{l=1}^{N_{prod,q}} R_{c,n_P(l,q),t} \qquad L_{c,q,i,t} = \sum_{l=1}^{N_{loss,q}} R_{c,n_L(l,q),t}$$

(19.41)

Gas conservation equation

$$\frac{\mathrm{d}C_{\mathrm{SO_2(g)},t}}{\mathrm{d}t} = -\sum_{i=1}^{N_B}\left\{k_{\mathrm{S(IV)},i,t-h}\left[C_{\mathrm{SO_2(g)},t} - S'_{\mathrm{S(IV)},i,t-h}\frac{c_{\mathrm{S(IV)},i,t}}{H'_{\mathrm{S(IV)},i,t-h}}\right] + P_{c,\mathrm{S(IV)},i,t} - L_{c,\mathrm{S(IV)},i,t}\right\}$$

(19.48)

Solving Aqueous Chemical Equations

Table 19.2. Reduction in array space and in the number of matrix operations before and after the use of sparse-matrix techniques for a case of growth coupled to aqueous chemistry

	Initial	After Sparse Reductions
Order of matrix	186	186
No. init. matrix positions filled	34596	1226 (3.5%)
No. final matrix positions filled	34596	2164 (6.3%)
No. operations decomp. 1	2,127,685	6333 (0.3%)
No. operations decomp. 2	17,205	1005 (5.8%)
No. operations backsub. 1	17,205	1005 (5.8%)
No. operations backsub. 2	17,205	973 (5.6%)