



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

An Aerosol Condensation Model for Sulfur Trioxide

K. E. Grant

February 8, 2008

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

An Aerosol Condensation Model for Sulfur Trioxide

Keith Eric Grant

29 February 2008

1 Introduction

This document describes a model for condensation of sulfuric acid aerosol given an initial concentration and/or source of gaseous sulfur trioxide (e.g. fuming from oleum). The model includes the thermochemical effects on aerosol condensation and air parcel buoyancy. Condensation is assumed to occur heterogeneously onto a preexisting background aerosol distribution. The model development is both a revisiting of research initially presented at the Fall 2001 American Geophysical Union Meeting [1] and a further extension to provide new capabilities for current atmospheric dispersion modeling efforts [2].

Sulfuric acid is one of the most widely used of all industrial chemicals. In 1992, world consumption of sulfuric acid was 145 million metric tons, with 42.4 Mt (mega-tons) consumed in the United States [10]. In 2001, of 37.5 Mt consumed in the U.S., 74% went into producing phosphate fertilizers [11]. Another significant use is in mining industries. Lawuyi and Fingas [7] estimate that, in 1996, 68% of use was for fertilizers and 5.8% was for mining. They note that H_2SO_4 use has been and should continue to be very stable.

In the United States, the elimination of MTBE (methyl tertiary-butyl ether) and the use of ethanol for gasoline production are further increasing the demand for petroleum alkylate. Alkylate producers have a choice of either a hydrofluoric acid or sulfuric acid process. Both processes are widely used today. Concerns, however, over the safety or potential regulation of hydrofluoric acid are likely to result in most of the growth being for the sulfuric acid process, further increasing demand [11].

The implication of sulfuric acid being a pervasive industrial chemical is that transport is also pervasive. Often, this is in the form of oleum tankers, having around 30% free sulfur trioxide. Although sulfuric acid itself is not a volatile substance, fuming sulfuric acid (referred to as oleum) is [7], the volatile product being sulfur trioxide. Sulfate aerosols and mist may form in the atmosphere on tank rupture. From chemical spill data from 1990-1996, Lawuyi02 and Fingas [7] prioritize sulfuric acid as sixth most serious. During this period, they note 155 spills totaling 13 Mt, out of a supply volume of 3700 Mt.

Lawuyi and Fingas [7] summarize information on three major sulfuric acid spills. On 12 February 1984, 93 tons of sulfuric acid were spilled when 14 railroad cars derailed near MacTier, Parry Sound, Ontario. On 13 December 1978, 51 railroad cars derailed near Springhill, Nova Scotia. One car, containing 93% sulfuric acid, ruptured, spilling nearly its entire contents. In July 1993, 20 to 50 tons of fuming sulfuric acid spilled at the General Chemical Corp. plant in Richmond, California, a major industrial center near San Francisco. The release occurred when oleum was being loaded into a nonfuming acid railroad

tank car that contained only a rupture disk as a safety device. The tank car was overheated and this rupture disk blew. The resulting cloud of sulfuric acid drifted northeast with prevailing winds over a number of populated areas. More than 3,000 people subsequently sought medical attention for burning eyes, coughing, headaches, and nausea. Almost all were treated and released on the day of the spill. By the day after the release, another 5,000 people had sought medical attention. The spill forced the closure of five freeways in the region as well as some Bay Area Rapid Transit System stations.

Apart from corrosive toxicity, there is the additional hazard that the reactions of sulfur trioxide and sulfuric acid vapors with water are extremely exothermic [10, 11]. While the vapors are intrinsically denser than air, there is thus the likelihood of strong, warming-induced buoyancy from reactions with ambient water vapor, water-containing aerosol droplets, and wet environmental surface. Nordin [12] relates just such an occurrence following the Richmond, CA spill, with the plume observed to rise to 300 m.

For all practical purposes, sulfur trioxide was the constituent released from the heated tank car. The behavior of the resulting plume suggested that initially sulfur trioxide behaved as a dense gas, but the chemical reacted with air humidity, producing sulfuric acid and heat. The heat caused the plume to rise. Eventually the plume cooled, resulting in sulfuric acid descending towards people on the ground. This kind of behavior is not accounted for in the popular gas dispersion models.

In the presence of complex terrain, such heat induced buoyancy could enable a sulfur trioxide cloud to leap local drainage boundaries with a single bound. Unless there were insufficient water/humidity to fully react with the SO_3 and H_2SO_4 on the first ascent, no secondary bounds would be expected, the cloud then behaving as a heavy tracer until sufficiently diluted.

2 Chemistry

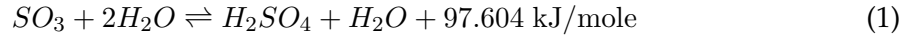
As noted by Steudel [16], the gas-phase reactions converting sulfur trioxide (SO_3) into sulfuric acid (H_2SO_4) are "surprisingly complex". The first order reaction of SO_3 with one water molecule has a high activation energy, resulting in reaction rates far below observations. The simplest reasonable reaction rate is from the second-order reaction, but higher order water complexes also contribute [5, 6, 9, 16]. Kolb et al. [6] note that the second order reactions explains an observed negative temperature dependence via the temperature dependence for formation of a water dimer. They also note that uncertainty exists whether H_2SO_4 is formed directly through the second order reaction or via formation of an intermediate $SO_3 \cdot H_2O$ adduct. Moreover, at high concentrations, SO_3 can condense directly onto H_2SO_4 forming disulfuric acid ($H_2S_2O_7$) [10]. Within droplets, H_2SO_4 may also not fully dissociate, depending on solution concentration [10].

In this investigation, we have considered only the second-order gas-phase reaction of SO_3 , ignoring the effects of larger water complexes. We have also ignored formation of disulfuric acid and incomplete dissociation of sulfuric acid in solution. However, to allow dry

condensation of SO_3 , we do treat SO_3 and H_2SO_4 as separate liquid species, the latter being rapidly formed from the former when sufficient free water is or becomes available in the droplet.

We also have not considered homogeneous nucleation for condensation of H_2SO_4 or coagulation of aerosol droplets as a growth mechanism. These two omissions are related. At low concentrations, the rate of homogeneous nucleation is orders of magnitudes less than condensation on existing particles. At extremely high concentrations, as might be achieved in a spill, the predominance of heterogeneous condensation may not be initially true. The many small particles thus created would grow initially, however, not by condensation on their surface, but by collision and coagulation. Homogeneous nucleation and coagulation would thus need to be considered as a linked system rather than as separate processes. Seinfeld [14] contains discussions of both processes. Small and Chuang [15] note the observational evidence for the importance of coagulation in cloud tops in transitioning from the nominal $10 \mu m$ cloud particle to the much large rain drop.

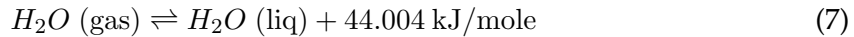
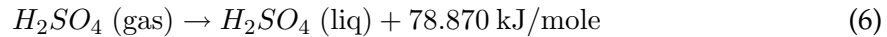
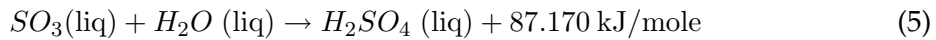
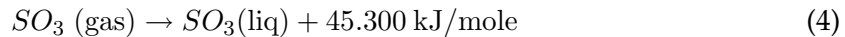
The microphysics includes two condensation paths from sulfur trioxide vapor to sulfuric acid in solution within aerosol droplets. The first path involves a gas phase reaction with water vapor to form sulfuric acid vapor. Research on activation energies and resultant rates indicate that this reaction involves two water molecules rather than one [5]. We include this second order concentration dependence, but have ignored the 5.4 kJ/mole involved with first forming and then breaking a water dimer.



$$\frac{d[SO_3]}{dt} = -k_1[SO_3][H_2O]^2 \quad (2)$$

$$\frac{d[H_2SO_4]}{dt} = k_1[SO_3][H_2O]^2 \quad (3)$$

The two condensation pathways are then the direct interaction of SO_3 molecules with droplets and the condensation of H_2SO_4 onto droplets. Additionally, water can condense or evaporate from the droplets.



The net difference between the two pathways is that the direct interaction of SO_3 with the droplet does not condense a water molecule – the water molecule, if available, is already in the liquid state or will subsequently condense independently. The increase in concentration of the solution will lower the vapor pressure of water at the surface of the drop, increasing condensation. Thus, the net difference may be as much one of bookkeeping as of end result. The net of converting one mole of SO_3 gas and one mole of water vapor to liquid H_2SO_4 176.474 kJ. There remains an additional 74.760 kJ/mole potentially available as a heat of dilution of H_2SO_4 .

Having the molar potential for energy release, allows making an estimate of the potential buoyancy effect. Consider an air parcel in which some dry air has been replaced by sulfur

trioxide. Assuming constant pressure, we can consider a virtual temperature for this parcel that would result in the same density as ambient air. Noting that the partial density for each component is given by $P M_i / (R T)$ and the sum of the partial pressures is the total pressure P , we have

$$\frac{1}{R T_v} [P_{SO_3} M_{SO_3} + P_w M_w + (P - P_{SO_3} - P_w) M_d] = \frac{1}{R T} [(P - P_w) M_d + P_w M_w] \quad (8)$$

$$\begin{aligned} T_v &= T \left[1 + \frac{P_{SO_3} (M_{SO_3} - M_d)}{(P - P_w) M_d + P_w M_w} \right] \\ &= T \left[1 + \frac{P_{SO_3} (M_{SO_3}/M_d - 1)}{P - P_w (1 - M_w/M_d)} \right] \end{aligned} \quad (9)$$

Under the approximation that $P_w \ll P$, the temperature difference simplifies to

$$\Delta T \equiv T_v - T = T \left[\frac{P_{SO_3} (M_{SO_3}/M_d - 1)}{P} \right]. \quad (10)$$

Per mole of air, the mole fraction of SO_3 is simply P_{SO_3}/P . The maximum available chemical energy will also depend on this mole fraction. Cancelling out the mole fraction from both sides, we can write an energy criterion for obtaining neutral buoyancy.

$$C_P T (M_{SO_3}/M_d - 1) < \Delta Q \quad (11)$$

where, ΔQ is the available reaction energy from a mole of SO_3 and C_P is the molar heat capacity.

The heat capacity of air is roughly 30×10^{-3} kJ/mole. The molecular weights for SO_3 and dry air are (roughly) 80 and 30, respectively. The left hand side of (11) evaluates to something on the order of 15 kJ/mole. We are more conservative in assuming that most of the water for reaction will have to already be in liquid droplets (e.g. fog) or will have to be evaporated and recondensed, thus using 132 kJ/mole for ΔQ rather than 176 kJ/mole. Given enough water, there is about eight times the available reaction energy needed for neutral buoyancy. This totally ignores energy of dilution. Given a moist environment, an air parcel would rise, as one of my undergraduate physics professors would say, "like a bat out of the west side of east Hades". Without sufficient water vapor, there is still the possibility of condensing SO_3 on H_2SO_4 to form $H_2S_2O_7$ (disulfuric acid). By itself, SO_3 has a latent heat of 45.3 kJ/mole. An additional perspective on the heating is that the presence of the sulfur chemistry decreases the saturation vapor pressure relative to the aerosol droplets. Thus sulfur-containing clouds will form/grow at higher than normal temperatures and the partial pressure of water vapor will be reduced (desiccation). A corollary is that, if an air parcel starts ascending, the condensation height will be lower than for clouds without SO_3 and H_2SO_4 content.

3 Aerosol Equations

In a simple parcel model involving only water condensation, the droplet volume, corrected for the dry aerosol volume can be used as a surrogate for the mass of liquid water. This

artifice was used in the most complete condensation/evaporation equations of Pruppacher and Klett [13] (henceforth simply PK)¹.

With a system including condensing species other than water vapor, the individual liquid species masses must be separately maintained. The particle growth equation thus becomes a diagnostic derived from the water and sulfuric acid mass contents and the density of the solution produced. Additionally, the heat release is now not simply a function of the rate of water condensation/evaporation but of water phase change, sulfur-trioxide deposition, sulfuric acid deposition, reaction of liquid sulfur trioxide with liquid water, and the heat of dilution of the sulfuric acid solution. For the particle radius, a , we have

$$\frac{1}{a} \frac{da}{dt} = \frac{1}{3} \left(\frac{1}{V} \frac{dV}{dt} \right) = \frac{1}{3} \left(\frac{1}{m} \frac{dm}{dt} - \frac{1}{\rho_{\text{asl}}} \frac{d\rho_{\text{asl}}}{dt} \right) \quad (12)$$

where, V is the droplet's volume, and m and ρ_{asl} are the droplet mass and density, respectively. The mass rate of change is simply the sum of the rates for the individual specie masses,

$$\frac{1}{m} \frac{dm}{dt} = (m_{\text{dry}} + m_w + m_{SA} + m_{SO_3})^{-1} \left(\frac{dm_w}{dt} + \frac{dm_{SA}}{dt} + \frac{dm_{SO_3}}{dt} \right) \quad (13)$$

Here, m_{dry} is the initial (and constant) mass of dry aerosol in each size of the droplets. Among other things, the presence of m_{dry} also ensures that (13) is not singular.

The density of the solution is evaluated as an empirical fit to standard data tables. This is given by,

$$\rho_{\text{asl}} = 1 + \frac{3.3990 \chi_{\text{stot}} (1 - 0.3647 \chi_{\text{stot}})}{1 + 1.6158 \chi_{\text{stot}}} \quad (14)$$

where, χ_{stot} is the combined mole fraction of H_2SO_4 and SO_3 . From this we have,

$$\frac{d\rho_{\text{asl}}}{d\chi_{\text{stot}}} = \frac{3.3990 (1 - 0.3647 \chi_{\text{stot}} (2 + 1.6158 \chi_{\text{stot}}))}{(1 + 1.6158 \chi_{\text{stot}})^2} \quad (15)$$

We can then express $d\chi_{\text{stot}}/dt$ in terms of the mole fractions and mole rates of change in a drop.

$$\frac{d\chi_{\text{stot}}}{dt} = \frac{1}{n} \left(\frac{dn_{\text{stot}}}{dt} - \chi_{\text{stot}} \frac{dn}{dt} \right) \quad (16)$$

Equations (15) and (16) thus provide a means for evaluating the time-derivative of the aerosol droplet density in (12). These equations do not account for the difference in density between pure sulfuric acid (1.83 g/cm³) and liquid SO_3 (1.92 g/cm³).

From PK², we can take an expression for the mass change of a droplet expressed as a diffusion current,

$$\frac{dm}{dt} = 4\pi a D_v^* (\rho_{v,\infty} - \rho_{v,\text{sat}}(T_a)) \quad (17)$$

where, D_v^* is a diffusion coefficient modified to include a gas kinetics correction for very small drops and $\rho_{v,\infty}$ and $\rho_{v,\text{sat}}(T_a)$ are the vapor density in the parcel and the saturation

¹PK, equation 13-26, p. 510

²PK, equations 13-9, 13-10, and 13-15b, pp. 504-506

density at the drop's surface, respectively. For water vapor, the possibility of evaporation and thus $\rho_{v,\text{sat}}(T_a)$ are important. For sulfur trioxide and sulfuric acid, however, saturation vapor pressures are extremely low. Thus we will approximate this term for these species while including it in more detail for water vapor.

Similar to the diffusion of mass onto the aerosol droplets, we can express the conductive heat transfer into a drop by ³

$$\frac{dq}{dt} = -J_{h,a} = 4\pi a k_a^* (T_\infty - T_a) \quad (18)$$

In this case, the heat involved is the total heat produced by condensation of all species and dilution of H_2SO_4 which is conducted into the air parcel environment from the aerosol drops. Thus we can write,

$$\frac{dq}{dt} = \sum_i L_i \frac{dm_i(\text{gas})}{dt} + \Delta H_{SO_3} \frac{d[SO_3(\text{liq})]}{dt} - \frac{dq_{dil}}{dt} \quad (19)$$

where, L_i are the latent heats of SO_3 , H_2SO_4 , and H_2O , ΔH_{SO_3} is the heat of reaction of liquid SO_3 with water, and dq_{dil}/dt is the rate of heat generation from dilution of H_2SO_4 . Equating (18) and (19), yields an expression for the droplet surface temperature,

$$T_a = T_\infty - \frac{1}{4\pi a k_a^*} \left[\sum_i L_i \frac{dm_i(\text{gas})}{dt} + \Delta H_{SO_3} \frac{d[SO_3(\text{liq})]}{dt} - \frac{dq_{dil}}{dt} \right] \quad (20)$$

and thus the relative increase in droplet surface temperature relative to the temperature of the surrounding air parcel

$$\delta \equiv \frac{T_a - T_\infty}{T_\infty} . \quad (21)$$

PK note that: ⁴

For usual conditions of drop growth $\delta \leq 10^{-5}$, which means that the heat released by condensation is very efficiently dissipated by conduction. One might therefore expect that the heating of the drop by release of latent heat could be ignored... However, this turns out not to be the case;... neglect of temperature differences between the drop and its environment leads to large errors for all sizes of drops and condensation nuclei.

In practice, this means that one can ignore the time for conduction to occur in treating the temperature response of the environment to heat production, but must include a term for the rate of heat production in modeling the rate of condensation/evaporation of water on the drop itself.

Thomsen [17] provides a function for the cumulative molar heat of dilution of H_2SO_4 as a function of the number of moles of water.

$$q_{1,dil}(n_w) = \left(\frac{74.76 \text{ kJ}}{\text{mole} \cdot H_2SO_4} \right) \left(\frac{n_w}{n_w + 1.7983} \right) \quad (22)$$

³PK, equations 13-19 and 13-20, pp. 508-509

⁴PK, p. 510

Where both the number of moles of water (n_w) and H_2SO_4 (n_{SA}) vary with time, (22) can be rearranged and differentiated to give

$$\left(\frac{dq}{dt}\right)_{dil} = \left[\frac{74.76 \text{ kJ}}{(n_w + 1.7983 n_{SA})^2}\right] \left[(n_w)^2 \frac{dn_{SA}}{dt} + 1.7983 (n_{SA})^2 \frac{dn_w}{dt}\right] \quad (23)$$

The variation of the saturation vapor pressure of water with temperature alone is obtained by integrating the Clausius-Clapyron equation.

$$\frac{d \ln e_{sat,w}}{dT} = \frac{L_w M_w}{RT^2} \quad (24)$$

Yielding,

$$e_{sat,w}(T_a) = e_{sat,w}(T_\infty) \exp \left[\frac{L_w M_w}{R T_\infty} \left(\frac{\delta}{1 + \delta} \right) \right] \quad (25)$$

Note that while, the latent heat L_w is that of water, the temperature difference between the drop surface and the environment can have a number of contributing components. First, however, we have to consider the changes in saturation vapor pressure from drop curvature and solution effects. PK give the expression (6.24a) for the drop curvature (surface-tension) effect.

$$\ln \frac{e_a}{e_{sat,w}} = \ln a_w + \frac{2M_w \sigma_{s/a}}{R T_\infty (1 + \delta) \rho_w a}, \quad (26)$$

where a_w is the chemical activity and $\sigma_{s/a}$ is the coefficient for surface-tension. In this case, a is used for itself, not as a mass surrogate, so it stands unaltered. In contrast, we have to back up from the final expression PK uses for a_w in (13.26), because they have assumed that the difference between the aerosol volume and the volume of the dry aerosol is all due to water. That doesn't fit the current need.

The importance of the activity to use is that it provides a direct measure of the equilibrium water vapor pressure over a real salt solution, or, in other words, the generalization of Raoult's law to real solutions. ⁵

If we work from PK (4.69), we can obtain

$$\ln a_w = -\nu_{SA} \Phi_{SA} \frac{1 - \chi_w}{\chi_w}, \quad (27)$$

where, ν_{SA} is the number of ions obtained from the dissociation of H_2SO_4 in solution and Φ_{SA} is the osmotic coefficient of H_2SO_4 . Thus, we can now put the parts together for the equation for saturation vapor pressure include effects of temperature, drop curvature, and solution effects. The effect of the osmotic coefficient is to further decrease the vapor pressure beyond the reduction due to decrease in mole fraction. There are further assumptions in our current treatment in ignoring partial dissociation of H_2SO_4 at high concentrations and resulting effects of ion production number and osmotic coefficient [10]. For initial prototyping, we are also using an osmotic coefficient fit for ammonium sulfate (already

⁵PK, p. 109

implemented) rather than one for sulfuric acid. Both solutions are hygroscopic, so the correction is in the right direction even if not quantitatively precise.

$$e_{sat,w}(T_a) = e_{sat,w}(T_\infty) \exp \left[\frac{L_w M_w}{R T_\infty} \left(\frac{\delta}{1 + \delta} \right) + \frac{2 M_w \sigma_{s/a}}{R T_\infty (1 + \delta) \rho_w a} - \nu_{SA} \Phi_{SA} \frac{1 - \chi_w}{\chi_w} \right] \quad (28)$$

Finally, this can be tied into a mass equation for the condensation and evaporation of water vapor in solution with H_2SO_4

$$\frac{dm_w}{dt} = \frac{4\pi a D_{v,w}^* M_w e_{sat,w}(T_\infty)}{R T_\infty} \left(S_{v,w} - \frac{1}{1 + \delta} \frac{e_{sat,w}(T_a)}{e_{sat,w}(T_\infty)} \right) \quad (29)$$

Equations (28) and (29) bring us to the same place in microphysics as PK's equation (13.26). The differences are that the water condensation is now framed in terms of water mass change rather than in terms of droplet radius change, calculation of the droplet surface temperature $T(a)$ involves multiple heating terms, and the ratio of saturation pressure at the drop surface to that in the environment is framed directly in terms of mole fraction of water rather than droplet radius.

For sulfuric acid and sulfur trioxide, we ignore the effects of curvature, surface tension and heating rate, treating only the supersaturation ratio. Yaws [18] provides temperature dependant fits for the vapor pressure of sulfuric acid and sulfur trioxide.

4 Parcel Equations

When used as part of a larger dispersion model, the microphysics and chemistry are simply included as another cell-based chemistry solver, with the outer model handling transport. As a stand-alone model air parcel model, equations for the properties of the parcel itself are needed. The vertical velocity W of the parcel is derived from the momentum equation given by

$$\frac{d(mW)}{dt} = g(m^* - m) - m g w_{asl} = gm \left(\frac{\rho_v^* - \rho_v}{\rho_v} - w_{asl} \right) \quad (30)$$

where, m^* is the ambient mass of air displaced by the parcel, ρ_v is the density of air in the parcel, ρ_v^* is the ambient air density, and w_{asl} is the mass mixing ratio of aerosol droplets in the parcel. Following PK, we account for acceleration of ambient air by including an 'induced mass' acceleration coefficient of $(1 + \gamma)$, where γ is generally taken to be 0.5. This is equivalent to assuming that the parcel has to accelerate about half its mass of ambient air in its motion.

The mass of the parcel increases by an entrainment rate proportional to the velocity.

$$\frac{dm}{dt} = \frac{dm}{dz} \frac{dz}{dt} = m \mu W \quad (31)$$

We use the base entrainment rate for a density bubble given by ⁶

$$\mu = \frac{0.6}{R} \text{sign}(W), \quad (32)$$

⁶PK, Equation 12-22, p. 495

with an additional user settable scaling factor. The entrainment coefficient must be the same sign as the velocity to insure that a descending air parcel continues to entrain air rather than detraining it. This correctly models a "buoyance oscillation" if the parcel rises quickly enough to overshoot its level of stability. Holton [4] notes that a typical tropospheric period for such oscillations, assuming a small initial displacement, is about eight minutes⁷.

It's interesting to note the form of (32) can be obtained by equating the Rayleigh drag force to the acceleration of ambient air mass being entrained.

$$F_D = -\frac{1}{2}\rho^*W^2AC_D = m^* \left(\frac{dW}{dt} \right)_D = \rho^*A(\alpha R) \left(\frac{dW}{dt} \right)_D \quad (33)$$

where, C_D is the drag coefficient and it's assumed that the volume of air entrained is given by the cross-section, A of the parcel times a height proportional to the parcel radius, R . Solving for the acceleration from drag gives

$$\left(\frac{dW}{dt} \right)_D = -\frac{C_D}{2\alpha R} W^2 \quad (34)$$

Comparison of (32) with (34) makes the connection, but with an additional concept. Not all of the air accelerated is necessarily entrained. Rather than resulting in entrainment, part of the drag acceleration could simply be spun off as turbulence into the environment through which the parcel is rising. We have, at least at this time, ignored this possibility in (35) immediately below.

With the various terms derived from (30) elaborated, the equation for the velocity can now be written as

$$\frac{dW}{dt} = \frac{g}{1+\gamma} \left(\frac{\rho_v^* - \rho_v}{\rho_v} - w_{asl} \right) - \frac{\mu}{1+\gamma} W^2, \quad (35)$$

again noting that μ must be given the same sign as W . The equations for the altitude and pressure of the parcel follow immediately,

$$\frac{dz}{dt} = W \quad (36)$$

$$\frac{d \ln P}{dt} = -\frac{g M_d W}{RT} \quad (37)$$

where, M_d is the molecular weight of dry air. The rate of temperature change of the air parcel depends on the vertical velocity, the fractional entrainment, and the total release of heat from condensation, reaction, and dilution.

$$\frac{dT}{dt} = -\frac{gW}{C_{pa}} + \mu W(T^* - T) + \frac{1}{C_{pa}} \frac{dq}{dt} \quad (38)$$

Having air for which the density varies with species content motivates not making the common replacement of density ratios with corresponding temperature ratios in (35)⁸. We must use a more general treatment. Having species abundances expressed in mass mixing

⁷Holton, p. 53

⁸Compare with PK, equation 12-25, p498

ratios (g-species / g-dry air), implies that the partial density of any species, ρ_x is simply proportional to the density, ρ_a of dry air, the proportionality factor being the mixing ratio.

$$\rho_x = w_x \rho_a \quad (39)$$

Combining (39) with the requirement that the sum of the partial pressures equals the total pressure give an expression for the density of dry air,

$$\rho_a = \frac{PM_d}{RT} \left[1 + M_d \sum_i w_i / M_i \right]^{-1} = \rho_d \left[1 + M_d \sum_i w_i / M_i \right]^{-1}, \quad (40)$$

where, ρ_d is the density that pure dry air would have at the given pressure and temperature. Finally, requiring the total vapor density, ρ_v to be the sum of the partial densities yields,

$$\rho_v = \rho_a \left[1 + \sum_i w_i \right] \quad (41)$$

Given (37) through (41), the density equation for the parcel follows.

$$\frac{d \ln \rho_v}{dt} = \frac{d \ln P}{dt} - \frac{d \ln T}{dt} + \sum_i \left[\left(\frac{M_i}{\rho_v} - \frac{M_d}{\rho_d} \right) \left(\frac{\rho_a}{M_i} \frac{dw_i}{dt} \right) \right] \quad (42)$$

The radius, R , of the parcel changes both with density and the entrainment of additional air.

$$\frac{d \ln R}{dt} = \frac{1}{3} \left(\mu W - \frac{d \ln \rho_v}{dt} \right) \quad (43)$$

The water vapor mixing ratio in the parcel, w_v is a balance between the loss/gain from all droplet condensation/evaporation and the moisture flux from entrainment of ambient air.

$$\frac{dw_v}{dt} = - \left(\frac{dw_L}{dt} \right)_{cle} + \mu W (w_L^* - w_L) \quad (44)$$

5 Computational Framework

5.1 Aerosol Size – Lagrangian vs. Eulerian

For the aerosol parcel model as a standalone program, parallelization is handled by duplicating the parcel evolution equations (pressure level, temperature, and parcel radius) on each processor and partitioning the size distribution bins over processors. An existing model, as LODI, however, is already handling transport and parallelization in terms of spatial regions. Thus the aerosol model can simply be treated as a scalar problem to be solved within each cell. In this, the logical framework and the code itself closely follows that for doing gaseous chemistry; a capability already tested within a LODI semi-Lagrangian framework.

In a stand-alone model, there is also the option of treating droplet-size evolution as either a Lagrangian problem or and Eulerian one. In the Lagrangian formulation, there are a fixed number of particles in each initial bin and the size of the bin itself changes over time

as a direct integration of (12). In the Eulerian treatment, droplet growth occurs by the movement of droplets between fixed size bins, with (12) providing the "velocity", v_a of such movements. We thus have an additional advection term to add to the droplet mass for each size. While mass will be conserved, the number of droplets will vary, being a diagnostic of the mass, the fixed droplet bin radius, and the solution density, the latter depending on the mole fractions. With those consideration, the droplet mass evolution is given by

$$\frac{\partial m_{SO_3}}{\partial t} + \frac{\partial (v_a m_{SO_3})}{\partial \ln a} + \frac{M_{SO_3} k_2}{N_0} [SO_3][H_2O] = \frac{4\pi a N_a D_{v, SO_3}^* M_{SO_3} P_{SO_3}}{R T_\infty} \quad (45)$$

$$\frac{\partial m_{SA}}{\partial t} + \frac{\partial (v_a m_{SA})}{\partial \ln a} - \frac{M_{SA} k_2}{N_0} [SO_3][H_2O] = \frac{4\pi a N_a D_{v, H_2SO_4}^* M_{SA} P_{SA}}{R T_\infty} \quad (46)$$

$$\begin{aligned} \frac{\partial m_w}{\partial t} + \frac{\partial (v_a m_w)}{\partial \ln a} + \frac{M_w k_2}{N_0} [SO_3][H_2O] &= \frac{4\pi a N_a D_{v, w}^* M_w e_{sat, w}(T_\infty)}{R T_\infty} \\ &\quad \left(S_{v, w} - \frac{1}{1 + \delta} \frac{e_{sat, w}(T_a)}{e_{sat, w}(T_\infty)} \right) \end{aligned} \quad (47)$$

One of the problems the advective scheme introduces, particularly if the number of size bins is small, is staying, simple, maintaining positivity, and not being so diffusive as to reduce the usefulness. Such a scheme was introduced by Leonard [8]. Leonard first reviewed oscillations introduced by central difference schemes and the diffusion introduced by a simple upstream scheme. He then notes, "However, by using a three-point upstream-weighted quadratic interpolation for each wall value individually a conservative formulation with stable convective sensitivity can be achieved. If the normal velocity component has the same sign for a given pair of opposite walls, a total of four nodal points per control-volume cell are involved in the respective coordinate direction. Diverging velocity components involve a centered three-point scheme, whereas converging velocity components involve five symmetrically placed points in the corresponding coordinate direction." We use the interpolation scheme to interpolate the droplet mass from centers to edges., after first taking a simple average of the velocities.

5.2 Solver

While chemical equations are typically framed as a set ordinary differential equations (ODEs), that formulation doesn't work for the equations presented above. The difference comes in the dependence of water condensation/evaporation on not only the solution itself, but the rate of heat release from the rates of reaction. The system is thus a set of implicit ODEs. We according use the IDA algebraic-differential equation solver to address this system. IDA is part of LLNL's SUNDIALS suite of solvers [3].

6 Results

The microphysics was tested in the stand-alone model formulation. Prior tests with the water only CAMP model [2] had been initialized with a parcel temperature 2 – 10° K above

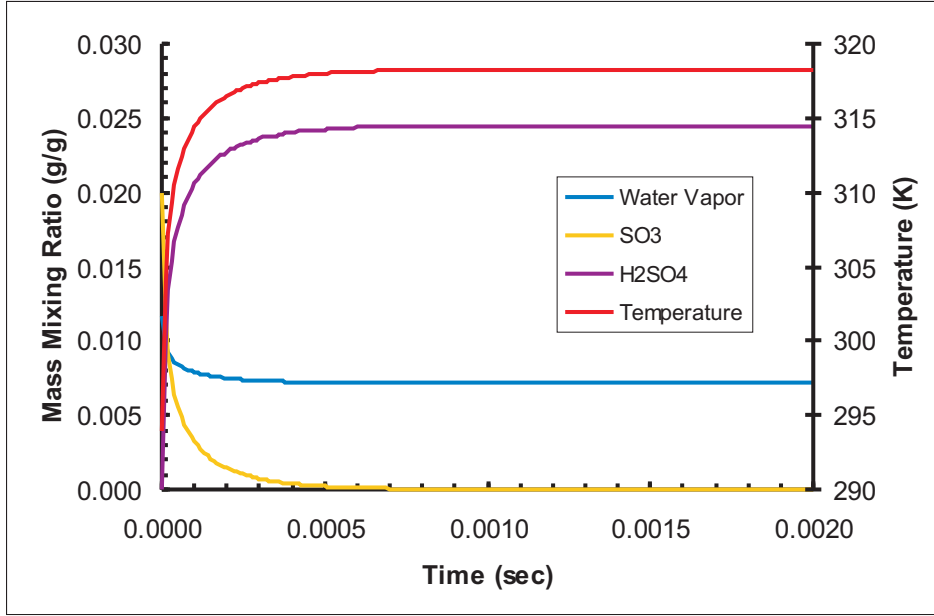


Figure 1: Conversion of SO_3 (gas) to H_2SO_4 (gas)

ambient air temperature to simulate heating from the ground and create initial buoyancy. For the current model, the interest was in initializing with an initial concentration of sulfur trioxide vapor and observing how heats of reaction, condensation, and dilution affected buoyancy.

Insight can be gained from adding only the reaction of SO_3 gas with water to form H_2SO_4 vapor, as in equation (1), to the basic parcel model. We choose a typical mid-latitude summer water mixing ratio of 1.17×10^{-2} (g/g) for water and a mixing ratio of 2×10^{-2} (g/g) for SO_3 . As shown by Figure 1, the conversion of SO_3 to H_2SO_4 is essentially complete within 2 milliseconds. The air parcel temperature increased by 24°K . These results were confirmed by hand estimates of reaction rates and energy release. The density ratio relative to moist air caused by the addition of H_2SO_4 is 1.024 while the density ratio due to the temperature increase is 0.923, resulting in a net density ratio, relative to ambient, of 0.946.

This simple mechanism test indicates an abundance of energy to create buoyancy, given typical ambient water vapor availability. It also indicates that the rate of parcel heating won't be limited by reaction rates, but by turbulent mixing of SO_3 into the air from an oleum or other source and subsequent turbulent mixing of generated heat to form a warmed parcel. When the size of the warmed parcel exceeds the scale of turbulent mixing, upward convection would occur.

7 Acknowledgments

This work was funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 05-ERD-050. Development of the computational/solver framework for an earlier version of the model described in this report was partly funded

by the Applied Math Program under the DOE Office of Advanced Scientific Computing Research via the Nonlinear Solvers and Differential Equations (NSDE) Project of LLNL's Center for Applied Scientific Computing (CASC). This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

References

- [1] Keith E. Grant, Catherine C. Chuang, Steven L. Lee, and Carol S. Woodward. Effects of aerosols on cloud properties – calculations with SensCAMP, a rising parcel model with parameter sensitivity analysis. Abstract, UCRL-JC-145309-ABS, Lawrence Livermore National Laboratory, December 2001.
- [2] Keith E. Grant, Catherine C. Chuang, Steven L. Lee, and Carol S. Woodward. Effects of aerosols on cloud properties – calculations with SensCAMP, a rising parcel model with parameter sensitivity analysis. Presentation, LLNL-PRES-401152, Lawrence Livermore National Laboratory, July 2007.
- [3] A. C. Hindmarsh, P. N. Brown, K. E. Grant, S. L. Lee, R. Serban, D. E. Shumaker, and C. S. Woodward. Sundials: Suite of nonlinear and differential/algebraic equation solvers. *ACM Transactions on Mathematical Software*, 31(3):363–396, 2005.
- [4] James R. Holton. *An Introduction to Dynamic Meteorology*. Academic Press, fourth edition, 2004.
- [5] John T. Jayne, Ulrich Pölschl, Yu min Chen, David Dai, Luisa T. Molina, Douglas R. Worsnop, Charles E. Kolb, , and Mario J. Molina. Pressure and temperature dependence of the gas-phase reaction of SO_3 with H_2O and the heterogeneous reaction of SO_3 with H_2O/H_2SO_4 surfaces. *J. Phys. Chem. A*, 101:10000–10011, 1997.
- [6] C. E. Kolb, J. T. Jayne, D. R. Worsnop, M. J. Molina, R. F. Meads, and A. A. Viggiano. Gas phase reaction of sulfur trioxide with water vapor. *J. Am. Chem. SOC*, 116:10314–10315, 1994.
- [7] Richard Lawuyi and Merv Fingas. *The Handbook of Hazardous Materials Spills Technology*, chapter 35: Sulfuric Acid. McGraw-Hill Professional, 2002.
- [8] B.P. Leonard. A stable and accurate convective modeling procedure based on quadratic upstream interpolation. *Computer Methods in Applied Mechanics and Engineering*, 19:59–98, 1979.
- [9] Thomas Loerting and Klaus R. Liedl. Toward elimination of discrepancies between theory and experiment: The rate constant of the atmospheric conversion of SO_3 to H_2SO_4 . *PNAS*, 97(16):88748878, 2000.
- [10] Hermann Müller. *Ullmann's Encyclopedia of Industrial Chemistry*, chapter Sulfuric Acid and Sulfur Trioxide. Wiley-VCH Verlag GmbH & Co. KGaA, 2005.
- [11] Thomas L. Muller. *Kirk-Othmer Encyclopedia of Chemical Technology*, chapter Sulfuric Acid and Sulfur Trioxide. John Wiley & Sons, 2006.

- [12] John S. Nordin. *The Handbook of Hazardous Materials Spills Technology*, chapter 17. McGraw-Hill Professional, 2002.
- [13] Hans R. Pruppacher and James D. Klett. *Microphysics of Clouds and Precipitation*. Kluwer, second edition, 1997.
- [14] John H. Seinfeld. *Atmospheric Chemistry and Physics of Air Pollution*. John Wiley & Sons, 1986.
- [15] Jennifer D. Small and Patrick Y. Chuang. New observations of precipitation initiation in warm cumulus clouds. *Journal of the Atmospheric Sciences*, (in press), 2008.
- [16] Ralf Steudel. Sulfuric acid from sulfur trioxide and water—a surprisingly complex reaction. *Angew. Chem. Int. Ed. Engl*, 34(12):1313–1315, 1995.
- [17] Julius Thomsen. *Thermochemistry*. Longmans, Green, and Company, 1908. Translated from the Danish by Katharine A. Burke, B.Sc (Lond); available online via Google Books.
- [18] C.L. Yaws. *Chemical Properties Handbook*. McGraw-Hill, 1999.